REMOVAL OF PHENOLIC COMPOUNDS FROM WATER USING NANO AND MICRO CARBON MATERIALS

BY

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DEDICATION

This work is dedicated to my beloved Parents, my wife, my brothers and my sisters

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In the name of Allah, the most Beneficent, the most Merciful.

All praises be to Allah, and the peace and blessings of Allah be upon his prophet, Mohammad (S.A.W)

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AC	:	raw activated carbon
AC-Ti	:	activated carbon impregnated with Titanium
AC-Al	:	activated carbon impregnated with Aluminum
AC-Fe	:	activated carbon impregnated with Irion
CNTs	:	raw carbon nanotubes
CNTs-Ti	:	carbon nanotubes impregnated with Titanium
CNTs-Al	:	carbon nanotubes impregnated with Aluminum
CNTs-Fe	:	carbon nanotubes impregnated with Irion
CNFs	:	carbon nanofibers
CNFs-Ti	:	carbon nanofibers impregnated with Titanium
CNFs-Al	:	carbon nanofibers impregnated with Aluminum
CNFs-Fe	:	carbon nanofibers impregnated with Irion
FA	:	fly ash
FA-Ti	:	fly ash impregnated with Titanium
FA-Al	:	fly ash impregnated with Aluminum
FA-Fe	:	fly ash impregnated with Irion
CP	:	cholorophenol
CBAs	:	Carbon Based Adsorbents
t	:	Adsorption Time
Dos	:	Adsorbent Dosage
M	:	modified

ABSTRACT

Full Name : **HAMZA ABBAS HAMZA ASMALY**

Thesis Title : **REMOVAL OF PHENOLIC COMPOUNDS FROM WATER USING NANO AND MICRO CARBON MATERIALS**

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This study was carried out to examine the power of carbon-based adsorbents include activated carbon, industrial fly ash, carbon nanotubes and carbon nanofibers in the removal of phenol and 4-chlorophenol (dangers of the human health) from the water. The system experiments conducted to obtain the ideal conditions to remove the highest ratio of phenol and 4-chlorophenol through the study of five variable elements, pH, the amount of dissolved material, contact time, mixing speed and the concentration of the dissolves pollutants in water. The affection of the impregnation metal oxides includes aluminum oxide, titanium oxide and iron oxide on the four carbon based adsorbent has been studied.

The results indicated that among all four adsorbents, the highest removal of phenol was observed to be 95% by using 100 mg activated carbon impregnated with aluminum oxide per 100 ml of solution at pH 7 and agitation speed 200 rpm during a time of two hours. On the other hand, the highest removal of 4-chlorophenol was observed to be 93% by using 100 mg of activated carbon impregnated with aluminum oxide per 100 ml of solution at pH 6, 150 rpm speed of mixing and 2 hours of contact time. This high removal efficiency of activated carbon refers to its special surface pours structure and its good response to the modification to its surface by impregnated metal oxides.

By applying the results of experiments, a mathematical equation representing the processes of adsorption and mechanical symmetric adsorption for each carbonic material from all used materials, in both states (raw and modified), have been developed. The adsorption capacities of phenol and 4-chlorophenol have been found on the surface of the four carbon adsorbents in both states (raw and modified) through these mathematical equations. The accuracy of the answers was completely identical with the conducted tests.

THESIS ABSTRAC (ARABIC)

ملـخــص الرسالـــــة

الاسم الكامل: حـمزة عـباس حـمزة عــصـملي

عنوان الرسالة: إزلـــة المركبات الفينولية من الماء باستخدام المواد الكربونية النانونية والمايكرونية

التخصص: هندســـــة كيمـــيائية

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هذة الدراسة أجريت لتحديد كفاءة الممتزات ذات الأساس الكربوني وتشمل الكربون النشط ,الرماد الصناعي, أنابيب النانو الكربونية والألياف النانونية الكربونية في إزالة الفينول ورابع كلوريد الفينول (الخطران علي صحة الإنسان) من المياة. أجريت منظومة التجارب للحصول علي الشروط المثالية لإزالة أعلي نسبة من الفينول ورابع كلوريد الفينول من خلال دراسة خمسة عناصر متغيرة وهي الرقم الهيدروجيني, كمية المادة المذابة ,الزمن ,سرعة الخلط وتركيزالفينول ورابع كلوريد الفينول الذائبين في الماء. وقد تمت دراسة أثر تشريب أسطح المواد الكربونية الممتزة الأربعة بواسطة كل من أوكسيد الألومنيوم ,أوكسيد التيتانيوم وأوكسيد الحديدك.وقد أوضحت النتائج أن أعلي نسبة لإزالة الفينول بلغت 95% وذلك باستخدام 100ملجم من الكربون النشط المتشرب بأوكسيد الألومنيوم لكل 100ملل من المحلول عند حامضية معتدلة 7 وسرعة خلط 200 دورة في الدقيقة خلال زمن قدرة ساعتين .في المقابل فإن أعلي نسبة إزالة لرابع كلوريد الفينول بلغت 93% وذلك و بإستخدام 100ملجم من الكربون النشط المتشرب بأوكسيد الألومنيوم لكل 100ملل من المحلول عند حامضية معتدلة 6 وسرعة خلط 150 دورة في الدقيقة وساعتان من الزمن. بإستخدام نتائج التجارب تم وضع المعادلات الرياضية الممثلة لعمليات الإمتصاص المتماثل وميكانيكية الإمتصاص الخاصة بكل مادة كربونية من المواد المستخدمة في كلا حالتيهم (العادية والمطورة). كما تم تحديد السعة الإمتصاصية لكل من الفينول ورابع كلوريد الفينول علي أسطح الممتزات الكربونية الأربعة في كلا الحالتين (العادية والمطورة) من خلال هذه المعادلات الرياضية. وقد كانت دقة النتائج متطابقة تماما مع التجارب التي أجريت.

CHAPTER 1

INTRODUCTION

1.1 General Introduction

In the recent decays, a great deal of attention has been required about the quality of fresh water in many countries over the world, due to the wide spread of the nemours organic compound contamination of the water resources which is growing rapidly from the development of chemical and petroleum industry. Different organic compound contamination such as benzene, toluene, ethyl benzene, phenol, nitro phenol and chlorophenol are the frequency encountered in the water resources especially in the ground water. Phenol and its byproducts considered to be high priority pollutants since they are harmful to both humans and animals. The effects of phenol in humans are similar to those produced in animals. Systemic absorption causes central nervous system impairment, kidney and liver damage, swallowing difficulty, anorexia, headache, fainting, dark urine and other mental disturbances [1].

There are many methods that were employed to treat water from phenol and its by-products in recent years such as, ozone generator technology, ion exchange, membranes and adsorption processes. However, in the treatment technology, it is essential to consider the most cost effective factor. The adsorption technology is wide spread of treat water from pollution, due to the high efficiently for removal of organics at trace level with low cost. Adsorption is a mass transfer process that involves contact of a solid (adsorbent) with a fluid containing the target solute (adsorbate). There are many alternative economical adsorbents used in many research to remove contaminations form water such as peat, rice husk, saw dust, clay and zolite. In all these types of adsorbents,

the surface area generally governs adsorption efficiency and selectivity as a result of accumulation of the adsorbates on the surface of the adsorbents [2].

Two promising alternatives for the selective removal of phenol and its by products are as follows, micro materials (Activated Carbon and Fly Ash) and nano materials (Carbon NanoTubes and Carbon Nano Fibers). The impact of nanotechnology on the development techniques to treat water from contamination will be more pronounced in the near future. Nanostructures of carbon materials was considered as important commercial materials since 1991, especially the (CNTs &CNFs) which take the first rank of the nanotechnology revolution in recent decade due to several good properties such as mechanical properties, high chemical stability and electrical prosperities. The important prosperity of these nano materials (CNTs &CNFs) is the higher ratio of surface area, in other words the surface area of the particle in nano scale level increase with decrease the particle size [3]. Part of this research is to continue the revolution for the application of nano materials in the water treatment fields.

The micro materials (AC and FA) are the second promising alternative to treat water from phenol and its by- products with low cost. Activated carbon is commonly used for purification of water from contamination due to its effective and excellent adsorbent. Activated carbon is characterized by its highly porous structure and widely different ranges of surfaces functional group. It also provides a large surface area range between 500 to 1500 m^2 /g, which enhance the adsorption of the contamination on its surface [4]. This is achieved through adsorption processes, where the atoms and molecules are fixed to the carbon surface via physical interactions or chemical bonds.

Fly ash is the second type of micro materials that have been employed in the recent years in the treatment of the water from the pollution. "Fly ash is one of the residues generated in combustion processes of coal and liquid fuels, and represents the fine particles that rise with the flue gases. The primary objective of using fly ash in construction and civil engineering application, as an additive to portland cements, is to find an application for the fly ash as environmental application for waste management "[5]. The classification of the fly ashes is based on their prosperities and the fuel source

which used to generate these ashes. Coal burning produces fly ashes with low content of unburned carbon. This type of fly ash is available with high percentages in South Africa. On the other hand, Liquid Fuel, such as heavy fuel oil, produces fly ashes with relatively high percentage of carbon content. The type of the fly ashes used in this study is produced from fuel oil processes, which is available in Saudi Industries. However, this type of fly ash is expected to be effective in the removal of the phenol and its byproducts due to the high percentage in the unburned carbon.

1.2 Significance of the Study

The solution to the environmental pollution in water can be achieved by all adsorbents based carbon due to the especial structure of carbon. Fly ash, activated carbon, carbon nanofibers and carbon nanotubes have been evaluated for the removal of contamination from the water and waste water. This study casts light on the effectiveness of removal of phenol and 4-chlorophenol at low initial concentration from water by using not only micro carbon materials such as, AC & FA but also nano carbon materials such as, CNTs and CNFs.

In addition, there are limited researches that delt with the treatment of the contamination of water and wastewater by using fly ash. The fly ashes which will be used in this research (liquid fly ash) have significant difference than the other fly ashes (coal fly ash) which were used in many previous researches. Therefore, this work will open new ways for treatment of water and wastewater from its pollution by using local fly ash generated from the industry plant in Saudi Arabia region such as Rabigh Electric Power which produces power from combustion of heavy oil.

Moreover, The enhancement of the removal efficiency of the contamination from water and wastewater have been studied in limited researches by using impregnation of ions such as Fe, Al and Ti on the surface of the adsorbents. This study should provide a new way in the enhancement of the removal efficiency of the carbon based adsorbents by using impregnation processes.

1.3 Objective of the Study

The main objective of this work of research is to obtain an economical adsorbent to treat contaminant water with phenolic compounds .The objectives can be summarized in the following:

1. To remove Phenol and 4 – Chlorophenol by using :
    a. Raw CNFs.
    b. Raw CNTs.
    c. Raw AC
    d. Raw FA (locally production).
2. To modify all carbon based adsorbents with metal oxide such as Al_2O_3, Fe_2O_3 and TiO_2 to enhance the removal efficiency of the phenol and 4-chlorophenol.
3. To optimize all processes parameter such as pH, agitation speed, contact time and dosage of the adsorbents, to maximize the removal of phenol and 4-chlorophenol from water.
4. To study the adsorption isotherm processes to describe the distribution of the adsorbate molecular between liquid and adsorbents using different models such as Freundlich and Langmuir adsorption isotherms.

CHAPTER 2

LITERATURE REVIEW

2.1 Activated Carbon

2.1.1 History of Activated Carbon

Activated carbon, also called activated charcoal, activated coal or carbo activatus, is a form of carbon that has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions. The word *activated* in the name is sometimes replaced with *active*. Due to its high degree of micro porosity, just 1 gram of activated carbon has a surface area in excess of 500 m^2, as determined typically by nitrogen gas adsorption. Sufficient activation for useful applications may come solely from the high surface area, though further chemical treatment often enhances the adsorbing properties of the material. Activated carbon is usually derived from charcoal [6].

Adsorption on porous carbons was described as early as 1550 B.C. in an ancient egyptian papyrus and later by Hippocrates and Pliny the Elder, mainly for medical purposes. In the 18th century, carbons made from blood, wood and animals were used for the purification of liquids. All of these materials, which can be considered as precursors of activated carbons, were only available as powders. The typical technology of application was the so-called batch contact treatment, where a measured quantity of carbon and the liquid to be treated were mixed, after a certain contact time, separated by filtration or sedimentation. At the beginning of the 19th century the decolourisation power of bone char was detected and used in the sugar industry in England. Bone char was available as a granular material which allowed the use of percolation technology, where the liquid to be treated was continuously passed through a column. Bone char, however, consists mainly of calcium phosphate and a small percentage of carbon; this

material therefore was only used for sugar purification. At the beginning of the 20th century, the first processes were developed to produce activated carbons with defined properties on an industrial scale. However, the steam activation and chemical activation processes could only produce powder activated carbon. During the First World War, steam activation of coconut char was developed in the United States for use in gas masks. This activated carbon type contains mainly fine adsorption pore structures suited for gas phase applications [7].

2.1.2 Classification of Activated Carbon

Activated carbons are complex products which are difficult to classify on the basis of their behavior, surface characteristics and preparation methods. However, some broad classification is made for general purpose based on their physical characteristics.

1. Powder Activated Carbon (PAC): Traditionally, active carbons which are made in particulate form as powders or fine granules less than 1.0 mm in size with an average diameter between 0.15 and 0.25 mm [8].
2. Granular Activated Carbon (GAC): its particle is large compare with the powder activated carbon consequently, presents a smaller external surface. This kind of activated carbon is used for water treatment, deodorization and separation of components of flow system. GAC can be either in the granular form or extruded and is designated by sizes such as 8×20, 20×40, or 8×30 for liquid phase applications and 4×6, 4×8 or 4×10 for vapor phase applications.
3. Extruded Activated Carbon (EAC): Consists of extruded and cylindrical shaped activated carbon with diameters from 0.8 to 45 mm. These are mainly used for gas phase applications because of their low pressure drop, high mechanical strength and low dust content.
4. Impregnated Carbon: These are porous activated carbons impregnated with inorganic elements such as iodine, silver, or cations such as Al, Mn, Zn, Fe, Li, and Ca.
5. Polymers Coated Carbon: This is a process by which a porous carbon can be coated with a biocompatible polymer to give a smooth and permeable coat

without blocking the pores, and the main application for this type is in the medical field.

6. Activated Carbon Cloth (ACC): This type is used by the military for Nuclear Biological Chemical (NBC) protective clothing, socks and gloves. It is also used in wound dressings, protective masks, for the protection of artifacts from tarnish and degradation, oil mist filters for compressors, gas sensors, electrodes, water purification, and more.
7. Biochar Activated Charcoal (BAC): this type is produced by a pyrolysis process with extremely low carbon emissions, a carbonization process that takes raw products straight through to the activation stage in less than an hour depending on the temperature range.

2.1.3 Properties of Activated Carbon

In general, the properties of the activated carbon are very important to determine if this type of AC is suitable or unsuitable for specific application. As example, ash and moisture content (Physical prosperities) can affect the use of a granular AC and render them either suitable or unsuitable for specific applications. Furthermore, the chemical properties such as specific surface area of activated carbon and surface chemistry is important for treatment of the contamination from water.

2.1.4 Methods of Production of Activated Carbon

The production of activated carbon can be achieved by two methods in general, by either steam or chemical activation. In both methods, the elevated temperature is required. The chemical activation is achieved often by dehydration of the raw material structure (cellulosic). On the other hand, the steam activation include removal of the volatile materials followed by oxidization of the carbon atoms.

2.1.4.1 Chemical activation

Recently, the raw material used in chemical activation is usually sawdust and activation agent such as phosphoric acid (most popular). In the past, the activation agents

that have been used were dehydrating agents, such as calcium hydroxide, calcium chloride, manganese chloride and sodium hydroxide. The chemical activation is achieved by mixed the raw material and reagent in a paste, dried and carbonized in rotary furnace at 600°C. In cause of using phosphoric acid as activation agent, the produce carbon heated to 800-1000°C during the oxidation of carbon by acid. Lastly, the activated product is washed by water and dried.

2.1.4.2 Steam activation

This type of activation can be applied to all raw materials. Numerous methods were developed to activate carbon by steam, but the basic steps of all these methods , is that an initial carbonation at 500-600 °C must followed by activation with steam at 800-1,1800°C.The processes is exothermic (converting carbon to carbon dioxide), so it possible to utilize this energy and have self –sustaining process.

$$C + H_2O \text{ (steam)} \longrightarrow CO + H_2$$

$$CO + \tfrac{1}{2} O_2 \longrightarrow CO_2$$

$$H_2 + \tfrac{1}{2} O_2 \longrightarrow H_2O \text{ (steam)}$$

$$C + O_2 \longrightarrow CO_2$$

2.1.5 Surface Functional Group of Activated Carbon

"The selectivity of activated carbons for adsorption is depended upon their surface chemistry, as well as their pore size distribution. Normally, the adsorptive surface of activated carbon is approximately neutral such as that polar and ionic species are less readily adsorbed than organic molecules [9]".

The surface functional groups on the activated carbon can be determine by numerous methods and attempts have been made to study the surface groups by spectroscopic methods, for examples by using infrared(IR). Figure 2-1 shows the several IR- active functional groups that may be found at the edges of and within graphene layers

after the processes of oxidative treatment of active carbon [9]. These functional groups are:

1) (a) aromatic c=c stretching , (b) and (c) carboxyl-carbonates.
2) (d) carboxylic acid , (e) lactone (4-membered ring).
3) (f) Lactone (5-membered ring).
4) (g) ether bridge , (h)cyclic ether.
5) (i) cyclic anhydride (5-membered ring).
6) (j) cyclic anhydride (6-membered ring).
7) (k) quinine
8) (l) Phenol.
9) (m) alchhol ,and (n)Ketene .

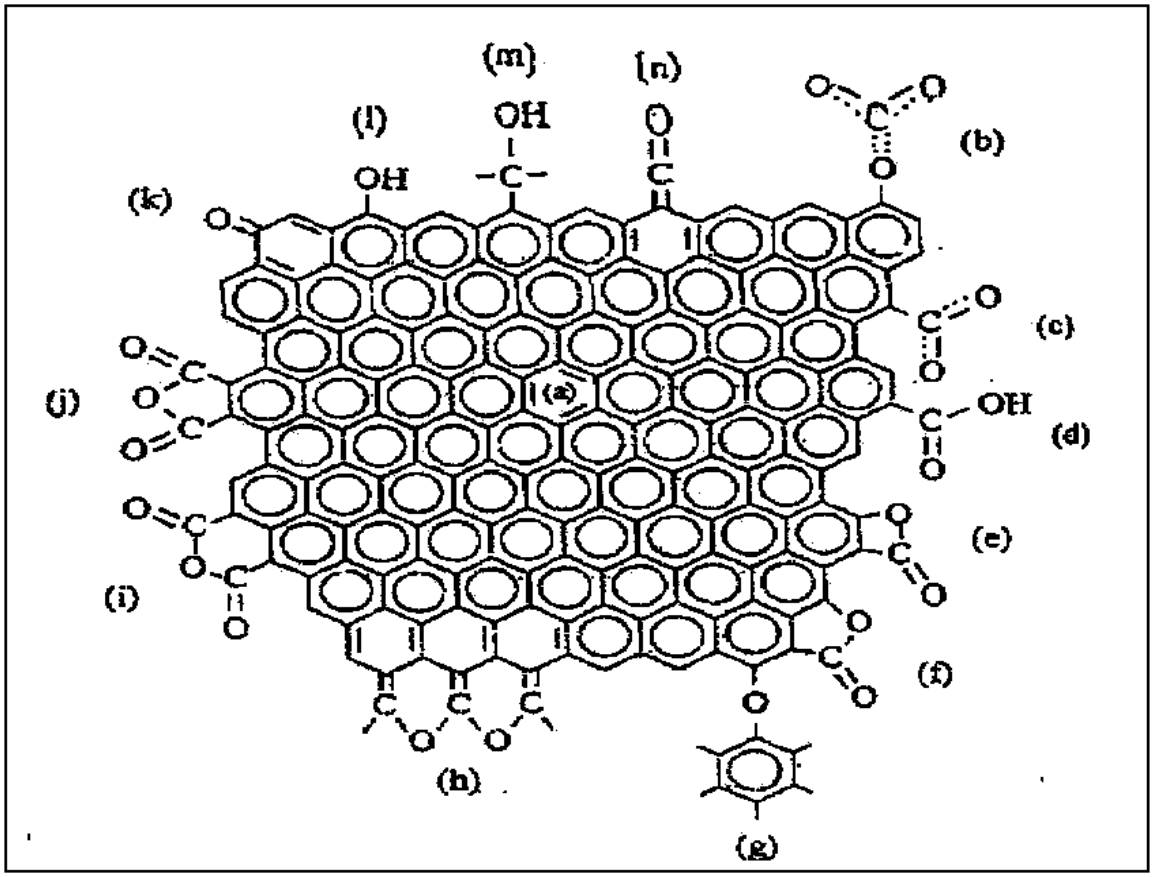


Figure 2-1 : IR-Active Functionalities on carbon Surfaces.

2.2 Fly ash

2.2.1 Background of Fly ash

Million tons of ashes (by product) have been created by the beginning of the 1920s as a result of the coal firing for power generation. In 2000, the estimation of fly ash reach up to 349 million tons produced worldwide [10]. Fly ash define by *'the finely divided residue that results from the combustion of ground or powdered coal and that is transported by flue gasses from the combustion zone to the particle removal system'*. [20]

Basically, fly ash is removed from the combustion gases by the dust collection system, either mechanically or by using electrostatic precipitators, before they are discharged to the atmosphere. Fly ash particles are typically spherical, finer than Portland cement and lime, ranging in diameter from less than 1 μm to no more than 150 μm [21].

The first application of fly ash was used as an additive to the Portland cement in the construction and civil engineering application [11].

Many reports on the field of wastewater and water treatment verify fly ash as a good adsorbents for toxic materials (organic compounds and heavy materials). The organic compounds include mercury, fluoride, phenol and methylene blue, while heavy materials include arsenic, boron, cadmium, lead, selenium, vanadium and many others [12].

Coal Fly ash has been used by Sen and De for removal of mercury from aqueous solution and they found it very effective in the adsorption processes. The pH of the solution was the most important parameter affecting the adsorption. They found that the optimum pH range was (3.5 – 4.5) [13]. A similar work was reported by Kappor and Viraraghavan [14].

Chaturvedi have studied the ability of fly ash to remove fluoride from water and wastewaters at different concentrations, times, temperatures and pH of the solution [15]. The rate constants of adsorption, inter particle transport, mass transfer coefficients and

thermodynamic parameters have been calculated at 30, 40, and 50^{o}C. At different concentration of the solution, the empirical models have been tested. He found that the removal of fluoride was achieved at low concentration, high temperature and acidic pH.

The use of coal fly ash for removal of methylene blue (MB) from aqueous solution was investigated by Yamada [16]. The adsorption of MB increased slightly and linearly with the increase in solution pH. The adsorption behavior strongly depended on the characteristics of individual fly ashes. Gupta also used fly ash to remove methylene blue from aqueous solution [17]. He found the percentage of removal of methylene was higher at high adsorbent concentrations.

2.2.2 Classification of Fly Ashes

The classification of the fly ashes depends on their properties and the source of fuel which are used to generate these ashes. Mainly, the fly ashes produced from the burning heavy fuel, containing three types of products of fly ashes [18]:

1. Fuel gas is a clean fuel, from which no ashes can be produced.
2. Liquid fuel, such as heavy fuel oil and this type of ashes is produced with average content percentages of carbon.
3. Coal burning which produce low content of unburned carbon fly ash.

The second types of fly ashes which produce from coal combustion can be classified into three types [19]:

1. Class C fly ash: produced from the burning of younger lignite or subbituminous coal, in the presence of water, it hardens and gains strength over time. Class C fly ash generally contains more than 20% lime (CaO).
2. Class F fly ash: produced from the burning of harder, older anthracite and bituminous coal. It contains less than 20% lime (CaO).
3. Class N fly ash: low in lime (CaO), with much high percentage of silica, alumina and iron [18].

2.2.3 Properties of Fly Ashes

According to Atsuko, the majority of fly ashes are alkaline and some of them are acidic [5]. Fly ash has a hydrophilic surface and porous structure similar to the activated carbon which makes it high efficiency adsorbent for contamination in the aqueous solutions.

In this research, we will only focus on using the heavy fuel oil fly ashes due to their availability with million tons in Saudi Arabia's industries. The fly ash produced from burning of heavy fuel oil in the power generation plant in Saudi, consolidated Electric Company in Rabigh, have been studied by M. A. Daous [22]. He found that, around 90% by weight of the ash consist of unburned carbon. However, this high rate of carbon expected to produce effective adsorption processes in water treatment filed.

The FA used in this research was collected from the Saudi Industry, the sample was analyzed by using (EDX) analysis, to know the exact percentage of unburned carbon of this sample of fly ash. Table 2-1 shows the percentage of the unburned carbon and the other elements on the fly ash.

Table 2-1 : EDX Analysis of FA

Element	Weight%	Atomic%
C	89.84	94.73
O	4.06	3.21
Al	0.97	0.45
Si	0.12	0.05
S	2.68	0.06
Ni	1.80	0.39
Cu	0.20	0.04
Zn	0.34	0.07
Total	100.00	

2.3 Carbon Nanotubes

2.3.1 What are Carbon Nanotubes

Carbon nanotubes are allotropes of carbon with a cylindrical nanostructure. Nanotubes have been constructed with length-to-diameter ratio of up to 132,000,000:1, which is significantly larger than any other material. These cylindrical carbon molecules have novel properties which make them potentially useful in many applications in nanotechnology, electronics, optics, and other fields of materials science, as well as potential uses in architectural fields. They exhibit extraordinary strength and unique electrical properties.

Nanotubes are members of the fullerene structural family, which also includes the spherical buck balls. The ends of a nanotube may be capped with a hemisphere of the buck ball structure. Their name is derived from their size, since the diameter of a nanotubes is on the order of a few nanometers (approximately 1/50,000 th of the width of a human hair), while they can be up to 18 centimeters in length [23].

2.3.2 History of Carbon Nanotubes

In 1996, a Nobel prize in chemistry was given to Harry Kroto, Robert Curl and Richard Smalley due to their discovery of entirely carbon atoms in special spherical tidy shape (Figure 2-2) [24]. However, due to the propinquity to the highly symmetric –scale structure, it was named "fullerene".

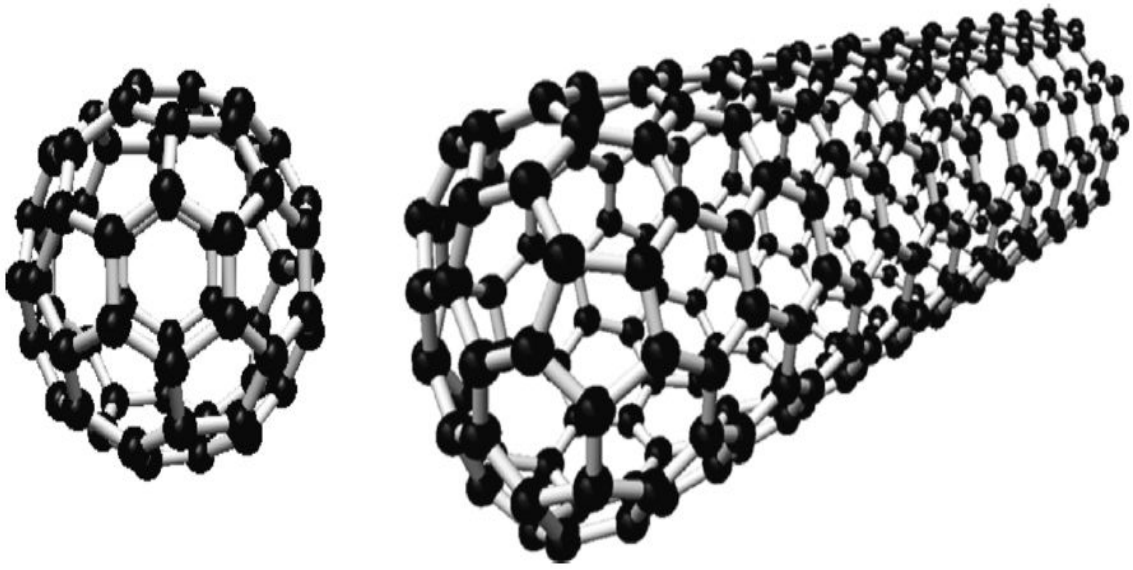


Figure 2-2 : Molecular models representing a C_{60} fullerene (left) and a single-walled carbon nanotube caped on one end (right).

An extensive research in the period from 1980 to 1990 was carried out on fullerene theory, synthesis, and its characterization. In 1991, transmission electron microscopy observations of elongated and concentric layered microtubules made of carbon atoms was presented by Iijima, these carbons had been considered as filamentous carbon. Recently, these carbons are called carbon nanotubes (CNTs) [25].

2.3.3 Classification of Carbon Nanotubes

Carbon nanotubes can be categorized by their structures into two main groups:

1. Single-Wall Nanotubes (SWNT)

Single-wall nanotubes (SWNT) are tubes of graphite that are normally capped at the ends. They have a single cylindrical wall. The structure of a SWNT can be visualized as a layer of graphite, a single atom thick, called graphene, which is rolled into a seamless cylinder. (Figure 2-3). Its diameter is close to 1 nm, tube length, can be many thousands of times longer. This graphene sheet when it is wrapped, it is represented by two indicators (n, m) called a chiral vector. These integers denoted the number of the unit

vectors through two directions in the honeycomb crystal lattice of graphene [26]. The structure of a Single-Wall Carbon Nanotubes (SWCT) is expressed as

$$V = n.a_1 + m.a_2$$

Where a_1 and a_2 are unit vectors.

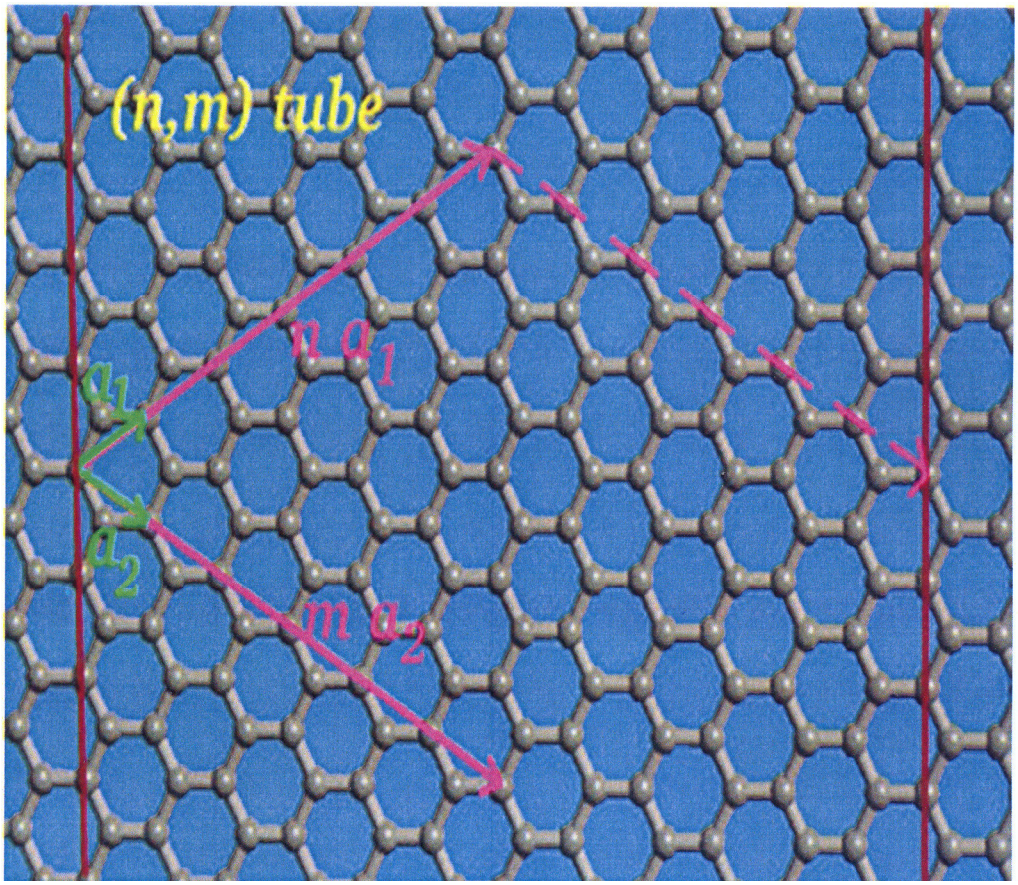
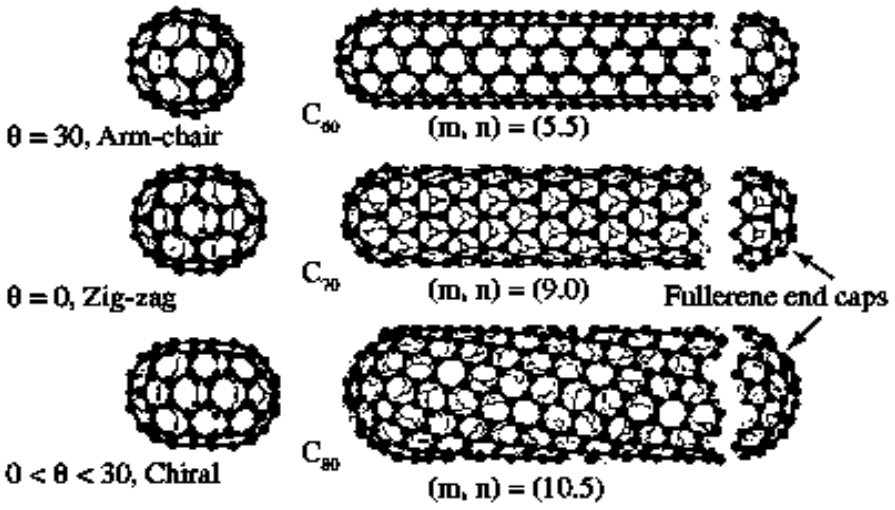
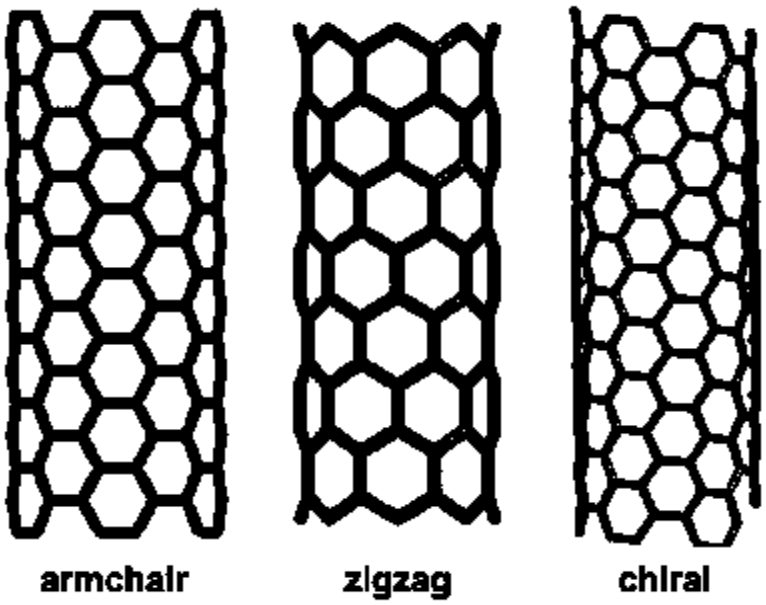


Figure 2-3 : Chiral vector in the Construction of the SMNT

When the value of m = 0, the SWNT called "zigzag", and when n = m this is called "armchair", otherwise the SWNT called "chiral"[27]. Figure (2-4 a &b) show the different types of the SWNT depending on the value of n, m and θ (Chiral angle) [27].



(a)



(b)

Figure 2-4 : Configuration of Single Wall NanoTubes Structures [28]

SWNT have unique electronic and mechanical properties which can be used in numerous applications, such as field-emission displays, nanocomposite materials, nanosensors, and logic elements. These materials are on the leading-edge of electronic fabrication, and are expected to play a major role in the next generation of miniaturized electronics.

2. Multi-wall Nanotubes (MWNT)

The second group of the Carbon nanotubes is multi-wall nanotubes, it appears either in the form of a coaxial assembly of SWNT similar to a coaxial cable, or as a single sheet of graphite rolled into the shape of a scroll (Figure 2-5).The diameter and the length are different from the SWCNT, so the property expect to be different also [29].

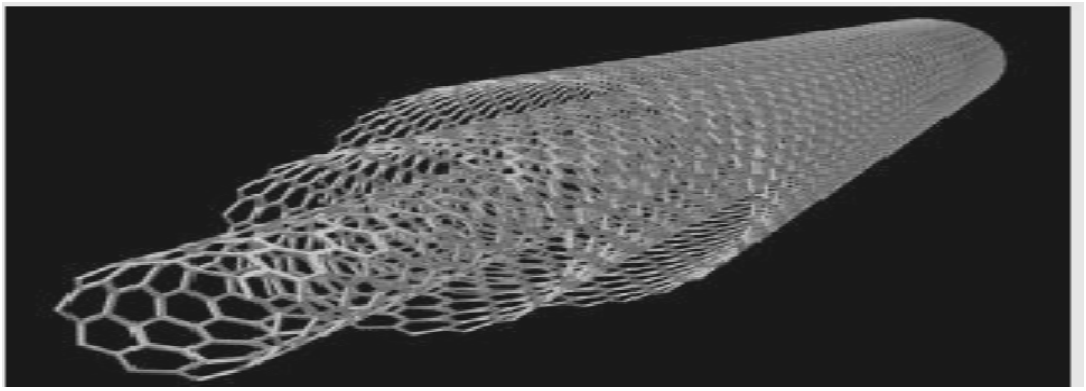


Figure 2-5 : Schematic Model for multiwall Nanotubes

2.3.4 Properties of Carbon Nanotubes

There are different types of properties of carbon nanotubes and they are as follows:

2.3.4.1 Thermal Properties

The thermal conductivity of carbon nanotubes is as good as that one of graphite and it depends on the temperature. The dependency of the thermal conductivity on the temperature was reported in 1999 by J. Hone, M. Whitney, and A. Zettle [30]. They found that the thermal conductivity has almost a linear relationship with the temperature. They suggested that the conductivity was linear in temperature from 7 K to 25 K. From 25 K to 40 K, the line increases in slope, and it arises monotonically with temperature to above room temperature. They developed a model to describe this relation, which is:

$$\mathbf{k}_{zz} = \sum \mathbf{C}\, \mathbf{v}_z^2\, \tau$$

Where:

$\mathbf{k}_{zz}$ is the slope of the line on the graph, **C** is the heat capacity, v is the sound velocity, and (τ)is the relaxation time, which is approximately 10^{-11} s. They also found that the thermal conductivity for a single rope at room temperature could vary between 1800 - 6000 W/m-K.

2.3.4.2 Mechanical Properties

Carbon nanotubes is one of the strongest materials (in terms of tensile strength and elastic modulus respectively) in nature, this fact referred to the strong covalent bonds between its atoms. In fact, CNTs are very strong in the axial direction [31]. The tensile strength of the multi-walled carbon nanotubes was tested in 2000 and it was measured up to 63 (GPa) [32] . The specific strength of the carbon nanotubes (48,000 KN. m. kg^{-1}) is the best materials known until now compared to high-carbon steel's 154 $KN{\cdot}m{\cdot}kg^{-1}$, Due to the low density of the carbon nanotubes which is in the range of 1.3 to 1.4 g/cm^3 [33]. The general mechanical properties of the different types of carbon nanotubes can be seen in Table 2-2 comparison with steel.

Table 2-2 : Comparison Mechanical Properties of different types of CNTs with steel

Materials	Young's Modulus (TPa)	Tensile Strength(GPa)	Density(g/cm^3)
SWNT	1 -5	13-53	2.6
Armchair SWNT	0.94	126.2	2.6
Zigzag SWNT	0.94	94.5	2.6
Chiral SWNT	0.92	-	2.6
MWNT	0.95	150	2.6
Stainless steel	0.214	1.55	7.8

2.3.4.3 Electrical Properties

The classification of the CNTs as either metallic or semiconducting is depends on its structure type, zig-zag, chiral or Armchair as clear in Figure 2-6. In generals for the given (n, m) if:

1. (n=m) the Nanotube is metallic .so all armchair nanotubes are metallic
2. (n-m is) amultiple of 3, the nanotube is semiconducting with a very small band gap.
3. Otherwise the nanotubes is a moderate semiconductor [34].

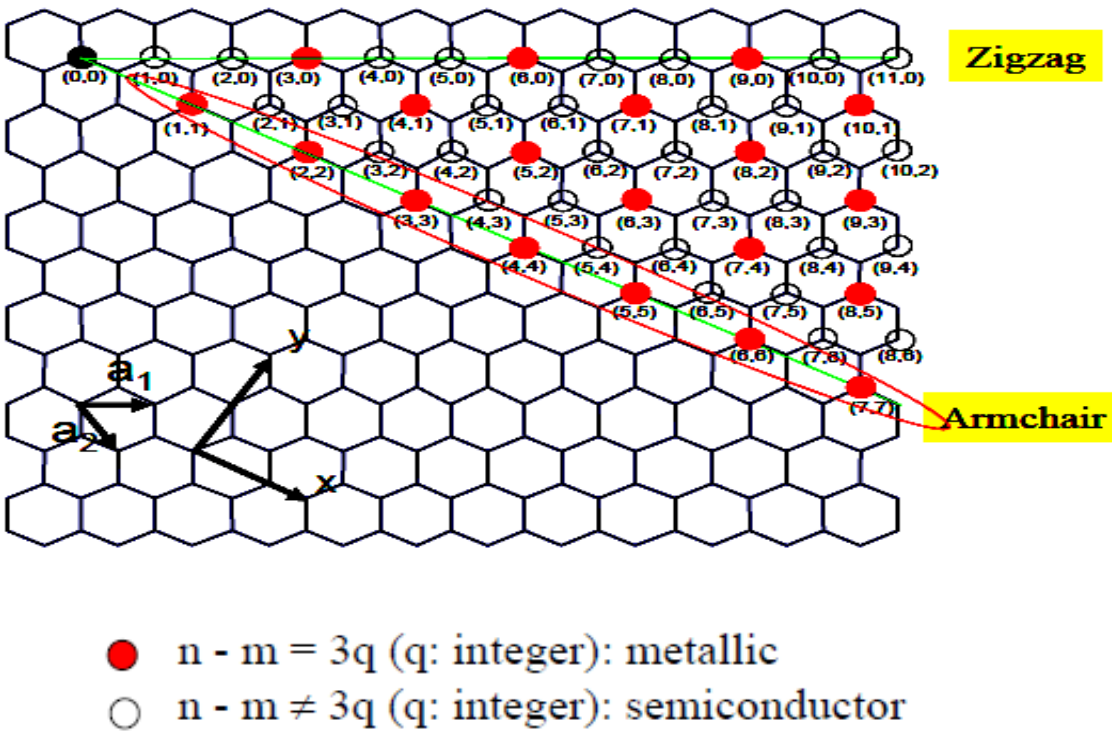


Figure 2-6 : Metallic and semiconductor CNTs [35]

2.3.5 Production of Carbon Nanotubes

There are nemours methods used to produce carbon nanotubes and many new routes were continuously being developed. The common and widely used today are:

1. Arc. Discharge Method

In this method higher temperature processes were used for the production of the carbon nanotubes as well as fullerenes. In fact, Arc Discharge method is probably one of the simplest methods for synthesizing nanotubes on a large scale. However, the simultaneous production of multi morphology, demands several purification steps.

In this method, an arc is ignited between two graphite electrodes in a gaseous background (usually argon/hydrogen) [36] (Figure2.7). The arcing evaporates the carbon and meanwhile it cools and condenses some of the product forms as filamentous carbon on the cathode. However, rabidly growth of the single –walled carbon nanotubes refer to the optimization of the metals in the anode [37]. This, in turn, stimulated the successful use of metal catalysts in other techniques for both single-walled and multiwall carbon nanotubes synthesis.

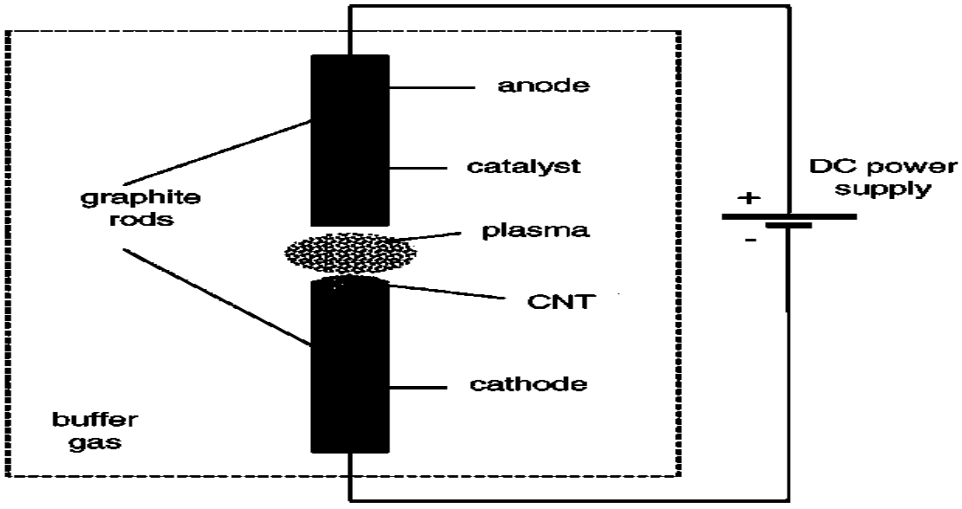


Figure 2-7 : Schematic diagram of an arc-discharge system

2. Laser Ablation

Historically, possibility of fullerenes synthesis of the carbon nanotubes by laser evaporation technique was reported by R.E. Smalley and his team work [38]. In this method, the laser light directed on the carbon surface in a stream of helium gas (Figure 2-8). Then, the evaporated material condenses on the surface of the reactor to produce MWCNTs. On the other hand, SWCNT with narrow diameter and high yield is

produced when using combination of a metal catalyst such as Co, Ni, and Fe in the carbon target [39].

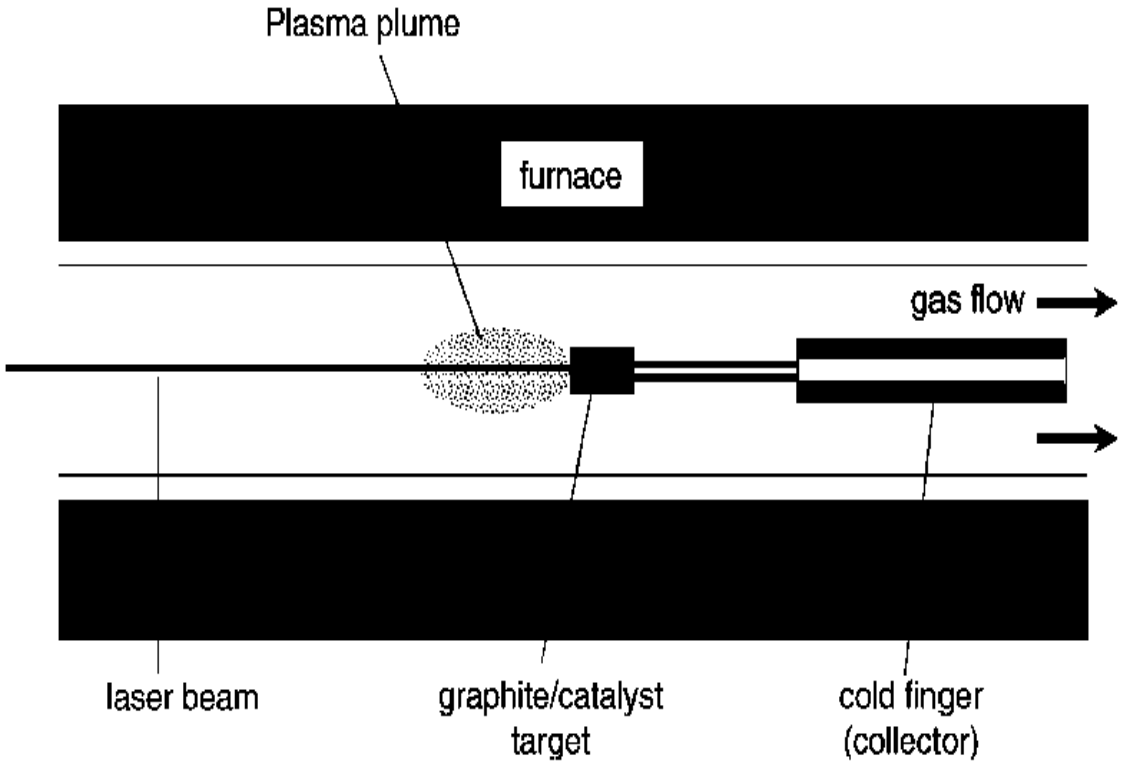


Figure 2-8 : Schematics Laser ablation set up

2.4 Carbon Nano fibers

2.4.1 What is Carbon Nanofibers

Carbon nano fiber is another member of the carbon family. Carbon nanofibers are cylindric nanostructures with graphene layers arranged as stacked cones, cups or plates. Carbon nanofibers with graphene layers wrapped into perfect cylinders are called carbon nanotubes. Sometimes carbon nano fibers called (VGCFs) vapor grown carbon fibers or (VGCNFs) vapor grown carbon nano fibers. The history of the carbon nanofibers dated back in 1889 when Hughes and Chamber [40] utilized a methane/hydrogen gaseous mixture and grew carbon filaments through gas pyrolysis and subsequent carbon deposition and filament growth. In 1950, Radushkevich and Lukyanovich able to show the hollow of the graphite carbon fibers diameter (50 nanometer) [41]. But, the exact

manufacture occurs in 1970 when Koyama and Endo succeeded in manufacture of CNFs with 1mm in length and1micrometer in diameter [42]. Today several companies produce carbon nano fibers in a comical scale production.

In addition, CNFs drew a lots of attention for its potential thermal, electrical, frequency shielding, and mechanical property enhancements.[43] In fact, it has being more and more utilized in different material systems like composites due to its exceptional properties and low cost [44].

2.4.2 Types of Carbon NanoFibers

The main types of CNFs structure include fishbone (herringbone), platelet, ribbon, and tubular structures (Figure 2-9) [45]. In fact, CNF nanostructures consist of graphite sheets oriented in a direction dictated by the growth process. The (Fishbone or herringbone) type possesses graphene layers stacked obliquely with respect to the fiber axis. The platelet CNFs consist of graphene layers oriented perpendicular to the growth axis. Lastly, ribbon CNFs are characterized by graphene layers that are parallel to the growth axis. These nanofibers were grown via catalytic decomposition of a carbon source over a metal catalyst composed of copper, iron, nickel, or a bimetallic compound.

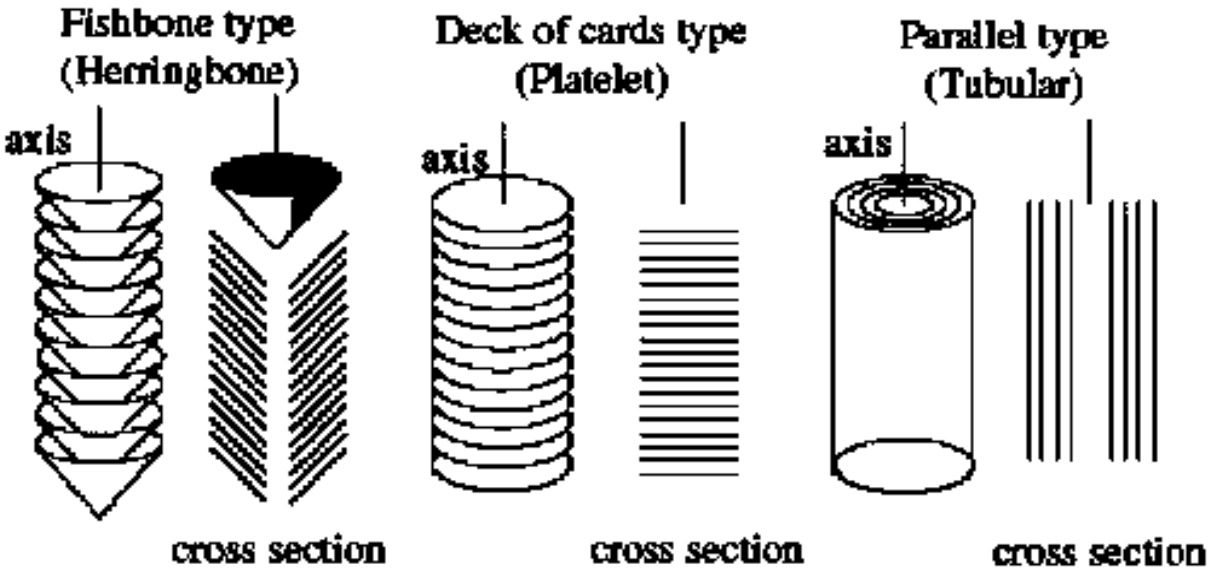


Figure 2-9 : Types of Carbon nanofibers

2.4.3 Properties of Carbon Nanofibers

Carbon nanofibers (CNFs) are discontinuous, highly graphitic, highly compatible with most polymer processing techniques, and they can be distributed in an isotropic or anisotropic mode [46]. CNFs have excellent mechanical properties, high electrical conductivity, and high thermal conductivity, which can be imparted to a wide range of matrices including thermoplastics, thermosets, elastomers, ceramics, and metals. Carbon nanofibers also have a unique surface state, which facilitates functionalization and other surface modification techniques to tailor/engineer the nanofibers to the host polymer or application. Carbon nanofibers are available in a free-flowing powder form (typically 99% mass is in a fibrous form) [47].

The modification of carbon nanofibers is similar to the carbon nanotubes. In general the modification can divide into three main types:

a. Non covalent adsorption of numerous functional atoms.
b. Covalent attachment of the chemical functional groups upon the reaction onto the skeleton of the CNFs.
c. The endohedral filling of carbon nano fibers inner empty cavity.

2.4.4 Production of Carbon Nanofibers

The methods used to create carbon nanotubes can be applied to synthesis of carbon nano fibers, but all reactions are catalytic. The important elements in the production of carbon nanofibers are a source of carbon and catalytic preparation stage. The general concept of the synthesis carbon nanofibers, that the catalytic synthesis of CNFs consists of the formation of these fibers on metallic catalysts in the form of powders, foils, gauzes, or supported particles. The procedure of production can summarize as follows:

a) Reducing the catalyst sample in a hydrogen-inert gas stream at a somewhat lower temperature. Followed by heating the catalyst up to the reaction temperature.
b) The reaction mixture which consists of hydrocarbon, hydrogen, and inert gas, is introduced into the system (Reactor) [48].

c) The reaction proceeds for periods ranging from a few minutes to several hours.
d) The suitable metallic used commonly is iron, cobalt, nickel, and copper.
e) The common sources of carbon materials (lower hydrocarbons) such as methane, acetylene, ethylene, benzene, and carbon monoxide.

The most common mechanism proposed in the literature for the production of CNFs consists of the hydrocarbons decomposition of the metal surface, releasing carbon atoms. Then, those carbon atoms form metal carbides which can be dissolved and diffused through the bulk of the metal, resulting in the deposition of CNFs at the other end of the metal particles [49, 50, 51]. Moreover, in recent years a new method developed by Tibbetts and Gorkiewicz [52] is used to synthesis CNFs. This method is called vapor-grown carbon nanofibers (VGCNF), a schematic of the (VGCNF) synthesis is shown in Figure(2-10). The summarized of the steps of (VGCNF) process are as follows:

a) A trace quantity of sulfur is added to the feed to promote the formation of CNFs. All the hydrocarbon feed, the catalyst and solvent, hydrogen gas, and a sulfur source, are fed into the reactor with electrical furnace to supply sufficient heat to maintain the pyrolysis temperature of 1,100 to 1,200^{o}C.
b) Iron pentacarbonyl ($Fe(CO)_5$) and Ferrocene ($C_{10}H_{10}Fe$), have commonly used catalyst sources.
c) The organ metallic catalyst decomposes, forming clusters of iron (Fe) particles that act as nuclei for the constitution and further growth of CNFs.
d) The fibers grow as they move along the reactor, and the diameter of fibers increases by the classic chemical vapor deposition (CVD) [53].
e) The fiber product comes out at the end of the reactor, along with the off-gases, trapped and separated via a series of cyclone separators or sometimes by using trap mechanisms which located downstream of the reactor.

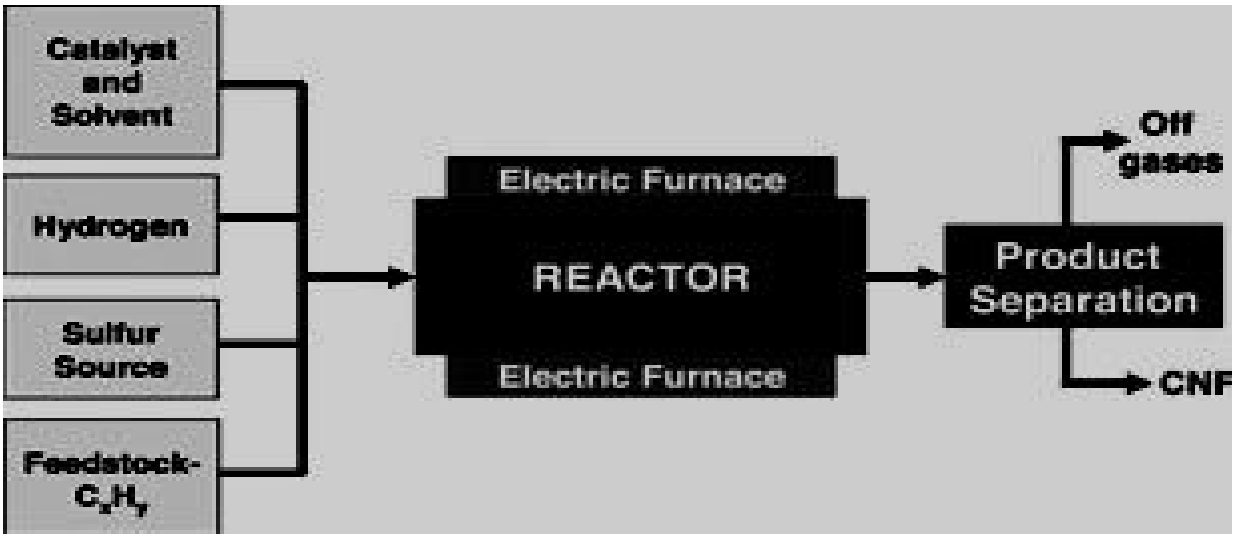
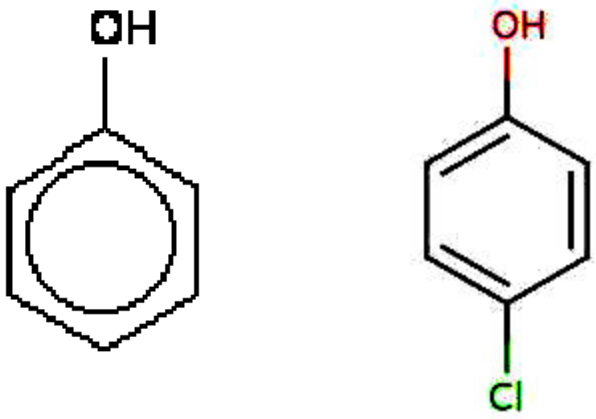


Figure 2-10 : Process schematic of vapor-grown carbon nanofiber (VGCNF) synthesis (The schematic is based on the process description by Tibbetts and Gorkiewicz)

2.5 Phenol and its Toxicity

Phenols belong to a class of organic compounds with aromatic functional groups (Figure 2-11) and their structures are similar to the more common herbicides and insecticides, which resist biodegradation. Pure phenol is a colourless, crystalline substance of characteristic odour, sweet, high solubility in organic solvent, oil carbon disulfide and water[70], it congeals into a solid at 41^0C .Phenol is very soluble in water and according to (U.S.EPA) its odour threshold is 0.04 ppm [54]. Chlorophenol is formed in the present of chlorine in the drinking water; it has a quite pronounced medicinal taste, and objectionable smell [55].



Phenol 4- Chlorophenol

Figure 2-11 : Molecular structure of adsorbates .

Phenols and its derivatives exist in the environment around us. Phenol can be found in air and ground water that is contaminated with the disposal products from the manufacture. Phenol in soil is likely to move to groundwater due to the fact that phenols are very mobile and can migrate to a considerable distance from its source [56]. The common sources of phenols in the wastewater are chemical and allied industries. Phenol can quickly escape down from the oil wheels, storage oil tanks and from the collapsed chemical plant due to any natural disaster through the soil system to the ground water. The most common anthropogenic sources of phenol in natural water include coal tar [57] and waste water from manufacturing industries such as resins, plastics, fibers, adhesives, iron, steel, aluminum, leather, rubber [58] and effluents from synthetic fuel manufacturing [59]. In fact, phenol is also released from pulp and paper mills and wood treatment facilities.

The synthesis of phenol on an industrial scale occurs by extraction coal tar as it is formed by transformation of high quantities of cumene present in plants that were used for tar production. Also, the reaction between chlorobenzene and sodium hydroxide is used to produce phenol. In addition, phenol is commonly used in various branches of industry including chemical – production of alkylphenols, cresols, xylenols, phenolic resins,

aniline and other compounds [60]. It is also used in pesticides, explosives, dyes and textile production [61].

The US Environmental Protection Agency (USEPA) recorded phenol as one of the first compounds inscribed into the List of Priority Pollutants. It reported phenol in their 1993 Toxic Release Inventory as one of the top twenty five chemicals that are most discharged by the US industries [62]. Due to the potential harmful of phenols (even in low concentration to organisms) to both human and animals, they have been classified as hazardous pollutants. The effect of phenol in animal is similar to that in humans. According to Farwell [63] and Sarkar [64] the systemic absorption causes central nervous system impairment, liver and kidney damage, difficulty in swallowing, anorexia, headache, fainting, dark urine and other mental disturbances. In many target regulatory, phenol have been listed as a contaminant of primary interest. The Ministry of Environment and Forests (MOEF), Government of India and EPA USA, have listed phenol and its by products on the priority – pollutants catalogue. The US Environmental Protection Agency (EPA) had call for lowering phenol content in waste water to 1.0 mg/l (1 ppm)[65]. The permissible concentration of phenol in the drinking water is 0.001mg/l(0.001ppm) according to World Health Organization (WHO)[66].

2.6 4- Chlorophenol and its Toxicity

Chlorophenol are groups of chemicals that are produced by adding chlorines (between one to five), so there are five basic types of chlorophenol; mono chlorophenols, die chlorophenols, tri chlorophenols, tetra chlorophenols and penta chlorophenols. The majority of chlorophenols are soild at room temperature and had very strong medical taste and smell. Chlorophenols are widespread in the environment and formed commonly by chlorination of mono and poly aromatic compounds present in water and soil [66]. The toxicity of the chlorophenol depends on the degree of the chlorination and the chlorine atoms position relative to the hydroxyl group. In other words, the toxicity of chlorophenols types is proportional with the number of the chlorine. So, we expected 4-chlorphenol to have higher toxicity than phenol itself. Chlorophenols are used in a

number of industrials and products. The expose to the high level can cause damage to the liver and to the immune system [67].

Chlorophenol is used as a pesticide and fungicide, a slimicide for paper mills, a preservative and a component in pentachlorophenol wood preservative. chlorophenol causes tract irritant to the nose, throat, and respiratory, corrosive to the eyes. It may cause skin burns, hyperthermia, methemoglobinemia, liver and kidney damage, and convulsions. Also, it may cause liver injury and chloracne [68]. Exposure to a mixture of 4-chlorphenols caused a plastic anemia in one adult [69].

2.7 Application of Carbon Based Adsorbents in water treatment

There were several methods that have been developed to remove phenol and its derivatives from water and wastewater, including electrochemical oxidation, iron exchange, chemical coagulation, solvent extraction, membrane separation, photocatalytic degradation and ozone technology [71-75]. The best method that has been used commonly for removal organic pollution as phenol and its by products from aqueous solution is adsorption technology due to its high removal efficiency, easy operation and economical compare to the above methods.

The adsorption process can be classified as chemical and physical adsorption. In the chemical adsorption, a reaction take place between the solid (adsorbent) and the adsorbate (solute), and the reaction is rarely used in water and wastewater treatment. On the other hand, the physical adsorption is widely used in water and wastewater, this type of adsorption is reversible processes and it is primarily due to van der waals' forces. The adsorption occurs due to greater attraction force between the adsorbent (as activated carbon) and adsorbate (as phenol). As a result of this attraction forces, the phenol molecular and its by products can easily adsorbed on the surface of the adsorbents such as activated carbon and fly ash [76].

In this research, the four based adsorbents were used to evaluate the affection of these materials on the removal of the low initial concentration of phenol and 4- chlorophenol from water. To maximize the removal, the processes parameters such as pH, agitation

speed, contact time and dosage of adsorbent were investigated. All these adsorbents were impregnated by (Al_2O_3, Fe_2O_3 and Ti O_2) to form hydroxyl groups on the surface of the adsorbents. A comparison between this modified forms and the regular carbon based adsorbents were studied to evaluate the effect of this modification on the removal efficiency.

In fact, the interaction between carbon atoms (Carbon based adsorbents) surfaces and the phenol molecular are still rather unknown and controversial [77, 78]. In previous researches some adsorbents were used to remove phenol and it by product from the aqueous solution, this works includes:

1. AC for removal phenol and 4- chlorophenol :

Activated carbon has been demonstrated as an excellent adsorption capacity for phenol and its derivatives like many other organic compounds. Riaz Qadeer et al, studied the removal of phenol from water by using activated carbon [79]. His study focused on the effect of shaking time, amount of the adsorbent and concentration of the adsorbate on the adsorption mechanism. The study carried out at room temperature (22 ± 1^0C), the concentration of phenol was measured by UV-visible spectrophotometer (Double beam, Shimadzu UV-160A) at wavelength 269 nm. According to the Riaz , the pH was fixed at 6.8 and 100% removal achieved by using 120 mg of AC at fixed parameter ; 10 ml volume , 10 min shacking time and phenol concentration 100 ppm (Figure 2-12). Also he studied the effect of initial concentration of phenol on the removal efficiency as shown in Figure (2-13)

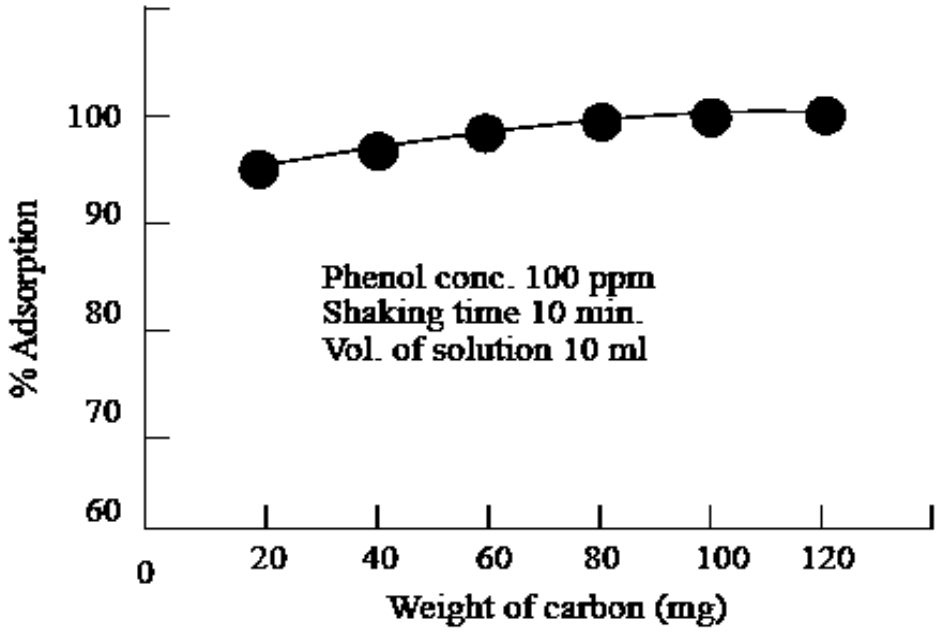


Figure 2-12: Influence of weight of activated carbon on phenol adsorption.

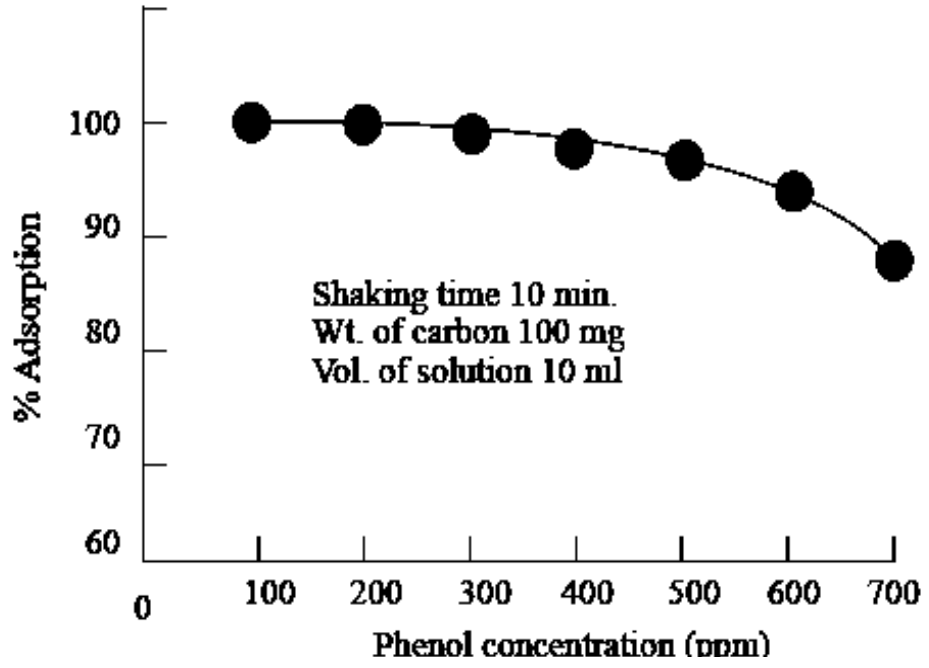


Figure 2-13 : Effect of phenol concentration on its own adsorption on the AC

Another study by Magdalena et, al. [80] on the removal of phenol from water by modified brown coal by nitrogen. The Brown coal was exposed to nitrogen in flow reactor at 300^0C for 2 hours. The study focused on the effect of phenol concentration on the adsorption capacity of the Brown coal. He took different initial concentration (100, 200, 300 and 500mg/l) in 250 ml volumetric flask. According to Magdalena, the increasing on the initial phenol concentration lead to significant increment on the adsorption capacity of the brown coal as shown in Figure 2-14. The equilibrium state chivied after 2 hours approximately, because after this time no vacant sites available on the surface of the adsorbent which means a saturation state occurred.

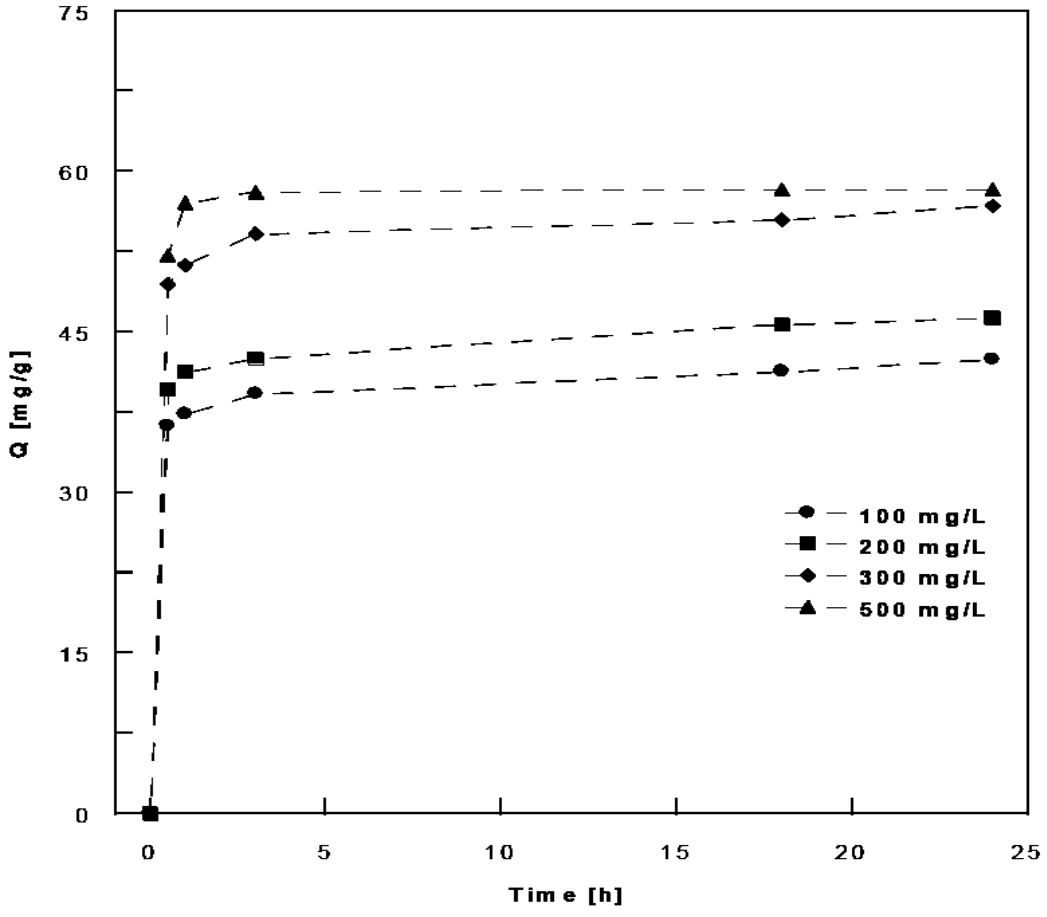


Figure 2-14 : Dynamic of phenol uptake by Brown Coal from various initial concentrations

Another study by Bakhtiar K et al. [81] on the removal of 4-chlorophenol from aqueous solution by using activated carbon on the oil Palm shell activated by K_2CO_3. The study carried out at (300 ^oC). The analysis of 4-chlorophenol concentration was determined by using Ultraviolet-Visible (UV-Vis) spectrophotometer (JASCO V-530). The study focused on the effects of solution pH, agitation time, and initial concentration .According to Bakhtiar, the highest removal of 4-chlorophenol reached (84.05%) at pH = 2, while the lowest removal (56.36%) occurred at pH=12, as can be seen from Figure 2-15. Also he found that, more than 10 hours were required attaining adsorption equilibrium for all different 4-chlorophenol solutions (Figure 2-16)

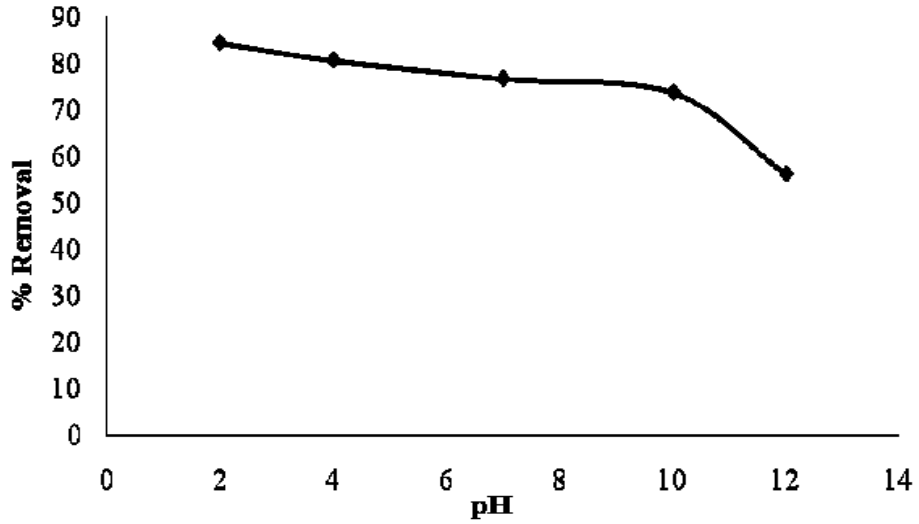


Figure 2-15 : Effect of the varying of pH on 4-CP removal by Oil Plasma Shell AC

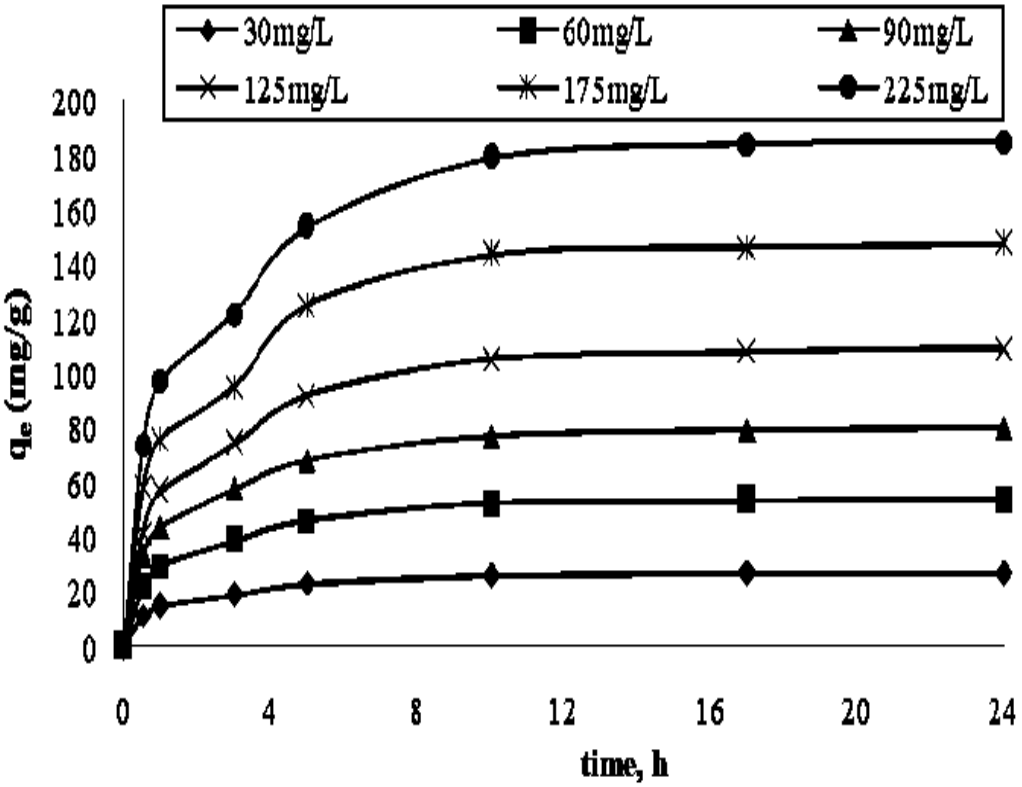


Figure 2-16 : Effect of Contact time on the adsorption of various concentrations of 4-CP on to Oil Plasma Shell AC

2. FA for Removal Phenol and Nitrophenols :

Samson et al. [82] studied the removal of phenol, 2-nitrophenol and 4-nitro- phenol from aqueous solutions by using coal fly ash. According to Samson, the fly ash used in his study was collected from Lethabo Power Station (South Africa). The study focused on obtaining new lowest cost adsorbent to remove phenol from water instead of activated carbon. The experimental parameters such as pH, contact time, dosage rate, were determined. The study was carried out at 34^{o}C in a fixed bed column to evaluate the dynamic adsorption behavior of phenol/FA through a dynamic column approach with length of 550 mm and internal diameter of 20 mm (Figure 2-17).According to the Samson, 90.2% removal of phenol was achieved at pH=2.22, contact time 22 h, 20 mg/l of phenol concentration and 40 g of activated carbon. The effect of activated carbon dosage can be seen in Figure (2-18)

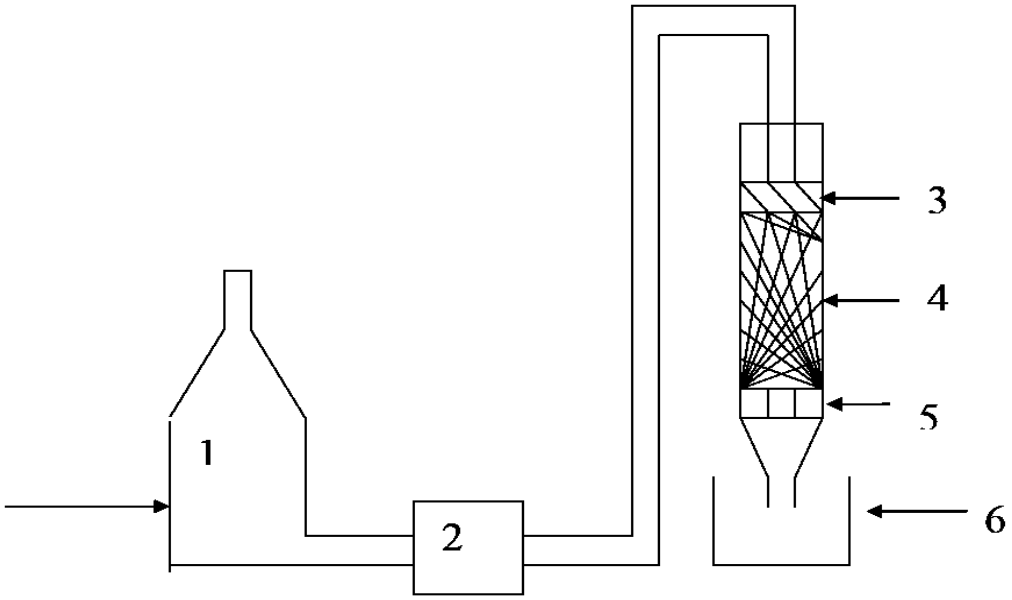


Figure 2-17 : Experimental diagram of down-flow packed column. (1) 20 mg/l adsorbate solution, (2) peristaltic pump, (3) glass beads, (4) FA, (5) glass beads, (6) effluent waste water

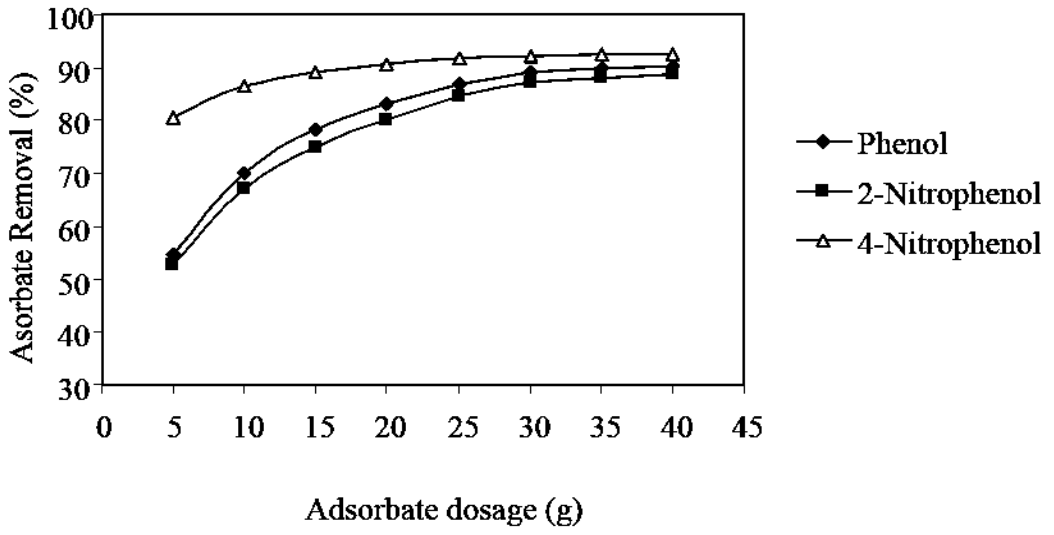


Figure 2-18 : Effect of adsorbents dosage on the removal of phenol, 2-Nitrophenl,4-Nitrophenol at pH 2.22,time 22h,C0 20mg/l and different loading weight of CFA(4-40)g

Also, Vimal et al. [83] studied the adsorption of phenol from water by fly ash .In this work, he focused on the operation parameters that affected the removal efficiency such as temperature, pH of the solution, contact time and the adsorption dosage. According to Vimal, the optimum conditions for phenol removal were found to be pH = 6.5, 10 g adsorbent dose, 50 ml stock solution, time ≈ 5h and 30^{o} C.

3. CNTs &CNFs for removal phenol and 4- Chlorphenol

The application of CNFs and CNTs reach attention in recent years on the water treatment area. CNT successes in many pervious work in the removal of heavy metal from water such as, the removal of (Cu, Co, Cd, Zn, Mn, Pb) from water by Anna Stafiej et al [84] and the removal of aniline from water by Hai Yan et al [85]. None of the previous work delt with the removal of phenol and 4-chlorophenol from water and wastewater by using carbon nano fibers.

2.8 Sorption Mechanism

The mechanisms by which the phenol and 4- chlorophenol molecular adsorbed on to the four carbon based adsorbents and their modified forms are very complicated. In fact, the interaction between the phenol molecular and the four carbon based adsorbents are still rather unknown and controversial [91]. All scientists believe that this specific interaction between the functional group (OH) on the phenol and 4-CP and surface of the carbon has great affection on the adsorption processes.

CHAPTER 3

METHODOLGY

3.1 Characterization of Adsorbents

The morphology of all adsorbents used in this research was characterized by using Scanning Electron Microscopy (SEM), Thermograph metric analysis (TGA), surface area and Porosity Analyzer (BET). Also, the (EDS) analysis was used to ensure that the impregnated materials exist on the surface of the adsorbents. In order to investigate the percent of the impregnation of materials on the surface of different adsorbents an Inductive Coupled Plasma Mass Spectrometer instrument (ICP-Ms) was used (Appendix B).

3.2 Preparation of Phenol and 4- Chlorophenol Stock Solutions

Firstly, all the laboratory glassware were washed carefully by using 2% of nitric acid to ensure the removal of any impurities on the glassware and prevent supplementary adsorption of phenol and 4-chlorophenol ions on the glassware walls.

Then, stock solution with concentration of 1000 ppm of phenol and 4-chlorophenol were prepared by dissolving 1000 mg of each element into 1.0 L of volumetric flask deionizer water and mixed very well by using magnetic stirrer. We were able to prepare any required concentration of phenol and 4-cholorophenol (100, 10, 8, 6, 4, 2ppm) by using dilution processes with the following relation

$$M_1V_1=M_2V_2$$

Where, the subscript "$_1$" refers to concentrated solution and the subscript "$_2$" refers to diluted solutions.

The prepared solutions were mixed gently to ensure proper mixing. The pHs of the stock solution were adjusted to the desired different values of pH by using 1.0M of NaOH for Base media and 1.0M of HNO_3 for acid media.

3.3 Batch Adsorption Mode Experiment

All the experiments in batch mode adsorption were conducted at room temperature to study the effect on initial solution pH, contact time, agitation speed and adsorption dosage on the adsorption of phenol and 4-chlorophenol. Each experiment was conducted in volumetic flask, with volume of 100 ml.

After each experiment, the solution was filtered by using Whatman No 11.5 filter paper, then by using UV-Spectrophotometer, a calibration curve was conducted by different concentration(2, 4, 6, 8 and 10 ppm). Finally, the concentration of the phenol and 4-chlorophenol was determined for each sample and obtained the removed amount of phenol and 4-chlorophenol.

3.3.1 Effect of pH

The effect of the pH of the solution on the removal efficiency of phenol and 4-chlorophenol from water was investigated by varying the value of pH from 3 to 8 and fixing all other parameter as show in Table (3-1)

Table 3-1 : Fixed Experimental Parameters

Experimental Parameter	Value
Initial Ion Concentration	2ppm
Solution Volume	100ml
Adsorption Dosage	50mg
Agitation speed	100 rpm
Contact time	2hr(120 min)

To adjust the solutions to the required pH, we used 1.0 M nitric acid to decrease the pH and 1.0 M of sodium hydroxide to increase the pH of the stock solutions.

3.3.2 Effect of Shacking Speed

The optimal pH of the phenol and 4-Chlorophenol removal was used to study the effect of the agitation speed of the ions removal keeping all other parameter constant, by each of the four adsorbents (AC, FA, CNTs and CNFs). The speed was varied from 50-250 rpm to reach the maximum diffusion of the ions towards the surface of all absorbents. All samples were shaken by mechanical shaker that is supported with digital controller to obtain accurate readings. Finally, all the samples were filtered by using Whatman No 11.5 filter paper and the remaining concentration were analyzed by using UV-Spectrophotometer.

3.3.3 Effect of Contact Time

The optimal pH and shacking speed as describe in the above two paragraphs were used to evaluate the effect of the contact time on the removal process of the ions from aqueous solution by each one of the four adsorbents. The experimental work was carried out at various duration time (10, 30 minutes, 1, 2 ,4 ,12 hr). Finally, after each experiment, the samples were filtered by using Whatman No 11.5 filter paper to remove the adsorbents and the remaining concentration was analyzed by UV-VIS-Spectrophotometer.

3.3.4 Effect of Adsorbent Dosage

From the above description, the optimum pH, agitation speed and contact time were used to evaluate the effect of the adsorbent mass on the maximum adsorption capacity of phenol and 4-chlorophenol for each of the four adsorbents (AC, FA, CNFs, CNTs). Therefore, the experimental work carried out for all different adsorbents in volume of 100 ml as following :10, 50, 100, 200, 300, 400, 500, 600 mg. Finally, after each experiment the adsorbents were removed by using Whatman NO 11.5 filter paper and the remain concentration of the solution was analyzed by UV-VIS-Spectrophotometer.

3.4 Experimental Design

The experimental model for this research work is shown in Table 3.2

Table 3-2 : Experimental parameters and its variation

pH	Shacking Speed (rpm)	Adsorption time	Dosage of Adsorbent(mg)
3	50	10 min	10
4	100	30min	50
5	150	1hr	100
6	200	2hr	200
7	250	4hr	300
8		12hr	400
			500
			600
			700

3.5 Impregnation of Ions on the Adsorbents

Impregnation of ions on the adsorbents becomes commonly used for the enhancement of the removal efficiency of the contaminated pollution from water stream. The impregnated ions lead to ion oxide production on the surface of the activated carbon which increase the adsorption ability of contaminant (chemical adsorption)[93]. The surface properties of the four based carbon adsorbents were modified by metal oxide such as AL_2O_3, TiO_2 and Fe_2O_3 according to following procedures:

a. Desired amount (5gm) of each adsorbent (AC, CNT, CNF and FA) was measured by using Mettler Toledo Balance. Impregnated materials (aluminum, titanium and Iron), were prepared from Aluminum Nitrate, Titanium isoprpoxide and Ferric Nitrate, respectively (Appendix B).
b. Each one of these chemicals (Ferric Nitrate, Aluminum Nitrate and Titanium isoprpoxide) was mixed with 5 gm of each one of the four adsorbents in 200 ml ethanol (purity 98%) in 500 ml flask and sonicated the mixtures for one hour by using Sonicator (110 volts at 40 % amplitude).

c. The mixtures were put on a hot plate for 48 hours under 70^0C to evaporate all ethanol .Then, the mixtures were washed 3 times (manual washing without using vacuum pump) to remove any ions that was not impregnated on the adsorbents (exist of this ions may affect the reading of the phenol concentration on the UV Spectrophotometer).
d. The mixtures were put in oven at 350°C for 3 hours to remove the excess of the (No_3) group from the four adsorbents.
e. All prepared adsorbents were kept and used to remove phenol and 4-chlorophenol.

3.6 Adsorption Isotherm Models

Adsorption Isotherm Models are one of the best mathematical model used to describe the distribution of adsorbate species among liquid and adsorbent surface. Langmuir and Freundlich isotherms are used for fitting the experimental data in adsorption studies to understand the extent and degree of favorability of adsorption.

The Langmuir model assumes [86]:

a. The surface of the adsorbent is in contact with a solution containing an adsorbate which is strongly attracted to the surface.
b. The surface has a specific number of sites where the solute molecules can be adsorbed.
c. All adsorption occurs through the same mechanism.
d. Adsorbed molecules (phenol and 4-chlorphenol in our case) do not interact.
e. The adsorption involves the attachment of only one layer of molecules to the surface, i. e. monolayer adsorption.

The Langmuir model is often expressed by:

$$\frac{C_e}{Q_e} = \frac{Q_m(K_L C_e)}{(1 + K_L C_e)} \text{ ---------- (1)}$$

Where:

Q_e = is the adsorption density at the equilibrium adsorbate concentration (mg of adsorbate per g of adsorbent).

C_e = is the equilibrium adsorbate concentration in solution (mg/l)

Q_m = is the maximum adsorption capacity corresponding to complete monolayer converge (mg of adsorbed per g of adsorbent).

K_L = is the Langmuir constant related to energy of adsorption (L of adsorbent per mg of a dsorbate) .

By linearization, equation (1) becomes:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad \text{----------(2)}$$

Equation (2) in a liner form can be used for linearization of the experimental data by plotting the value of $(\frac{C_e}{Q_e})$ againstC_e, and the Langmuir constant (Q_m, K_L) can be evaluated from the slope and the intercept, respectively.

The second equation that is used to describe the adsorption isotherm is Freundlich model which can be used if there is a good liner fit, and it expressed by:

$$Q_e = K_F (C_e)^{1/n} \quad \text{----------(3)}$$

Where:

Q_e = is the Adsorption density (mg of adsorbate per g of adsorbent).

(C_e) = is the concentration of adsorbate in solution (mg/l).

K_f and n are the empirical constant depending on several environmental factors and n greater than one. By taking the log of equation (3), a liner form can generated as:

$$\mathbf{Log}\, Q_e = LogK_f + \left(\frac{1}{n}\right) Log(C_e) \text{----------(4)}$$

By plotting log (C_e) against $Log(C_e)$ a straight line which indicates the best confirmation of the Freundlich isothermal for adsorption is formed. The value of (1/n) represents the slope and $Log\ K_f$ is the intercept.

3.7 Kinetic Modeling

Sorption kinetics will be applied to describe the removal rate of the adsorbate, which also describes the residence time of the adsorbate at the interface between the solid and liquid. To evaluate the mechanism of sorption of phenol and 4-chlorophenol by all carbon based adsorbents, the following equations were applied:

a. The first order equation:

$$Log\frac{Q_e - Q_t}{Q_e} = -\frac{K_L\ t}{2.303} \text{----------(5)}$$

The calculated quantities of log $(Q_e - Q_t)$ will be plotted versus time (t).

b. The pseudo –second order rate equation :

$$\frac{t}{Q_t} = \frac{1}{2K_s Q_e^2} + \frac{t}{Q_e} \text{----------(6)}$$

The calculated quantities $(\frac{t}{Q_t})$ will be plotted versus time (t).

c. The Second order rate equation :

$$\frac{1}{Q_e - Q_t} = \frac{1}{Q_e} + K_2 t \text{----------(7)}$$

The calculated quantity $(\frac{1}{q_e - q_t})$ will be plotted versus time (t).

Where:

Q_e = Sorption Capacity at equilibrium.

Q_t = Sorption Capacity at time (mg/g).

K_L= the lagergren rate constant of adsorption (min^{-1}).

K_2 =Rate constant of the pseudo second –order sorption ($g.mg^{-1}.min^{-1}$)

t = Time (min)

The respectively kinetics model for each adsorbent will be determined from the best fit for the liner equations from the above three equations.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Adsorbents Characterization

4.1.1 Scanning Electron Microscopy (SEM).

The carbon nanotubes, carbon nanofibers, activated carbon and carbon fly ash were characterized by scanning electron microscopy (FE-SEM). Figure 4-1 shows the SEM images of carbon nanotubes(a ,b), carbon nanofibers (c, d), while Figure 4-2 shows the SEM images of activated carbon(e, f) and fly ash (g, h)respectively. The diameters of the produced carbon nanotubes vary from 20 nm to 40 nm with an average diameter of 24 nm while for carbon nanofibers vary from 100-250 nm. The size of activated carbon vary from 600 – 1000 micron, while in case of fly ash, its size vary from 500 -1500 micron. The SEM image of FA compared to the activated carbon demonstrates the high surface area of the FA and its potential for use as adsorbent. One important feature of FA over other carbon based adsorbents is the high content of metals which help in speeding and magnifying the adsorption.

The SEM images of the modified adsorbents were also taken. We focused on the images of the modified adsorbents by aluminum metals due to its high removal efficiency than the other modified adsorbents by titanium and irons. Figure 4-3 shows the images of the FA-Al, AC-Al, CNT-Al and CNF-Al, respectively.

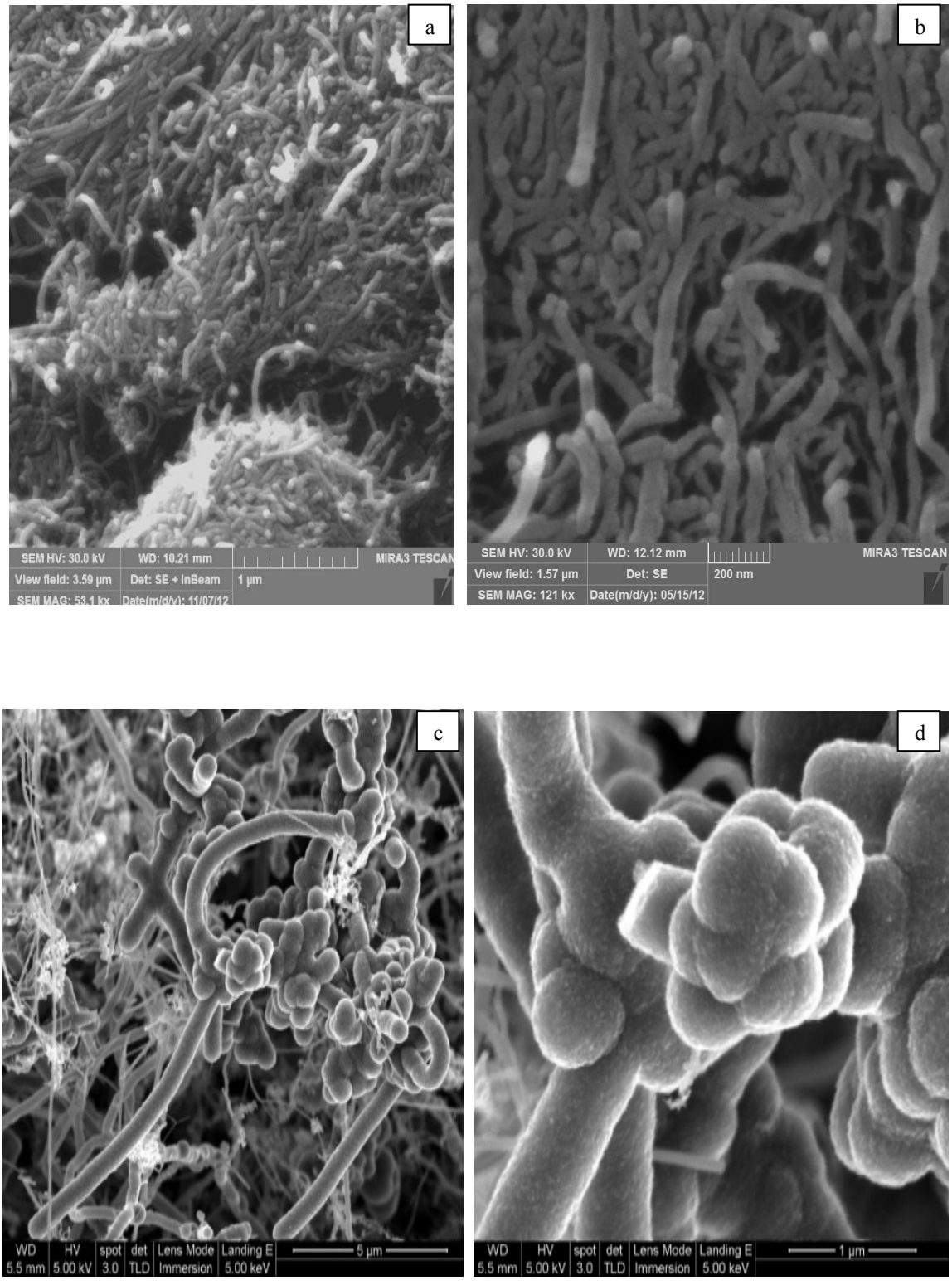


Figure 4-1: SEM image of CNT (a, b) and CNF(c, d)

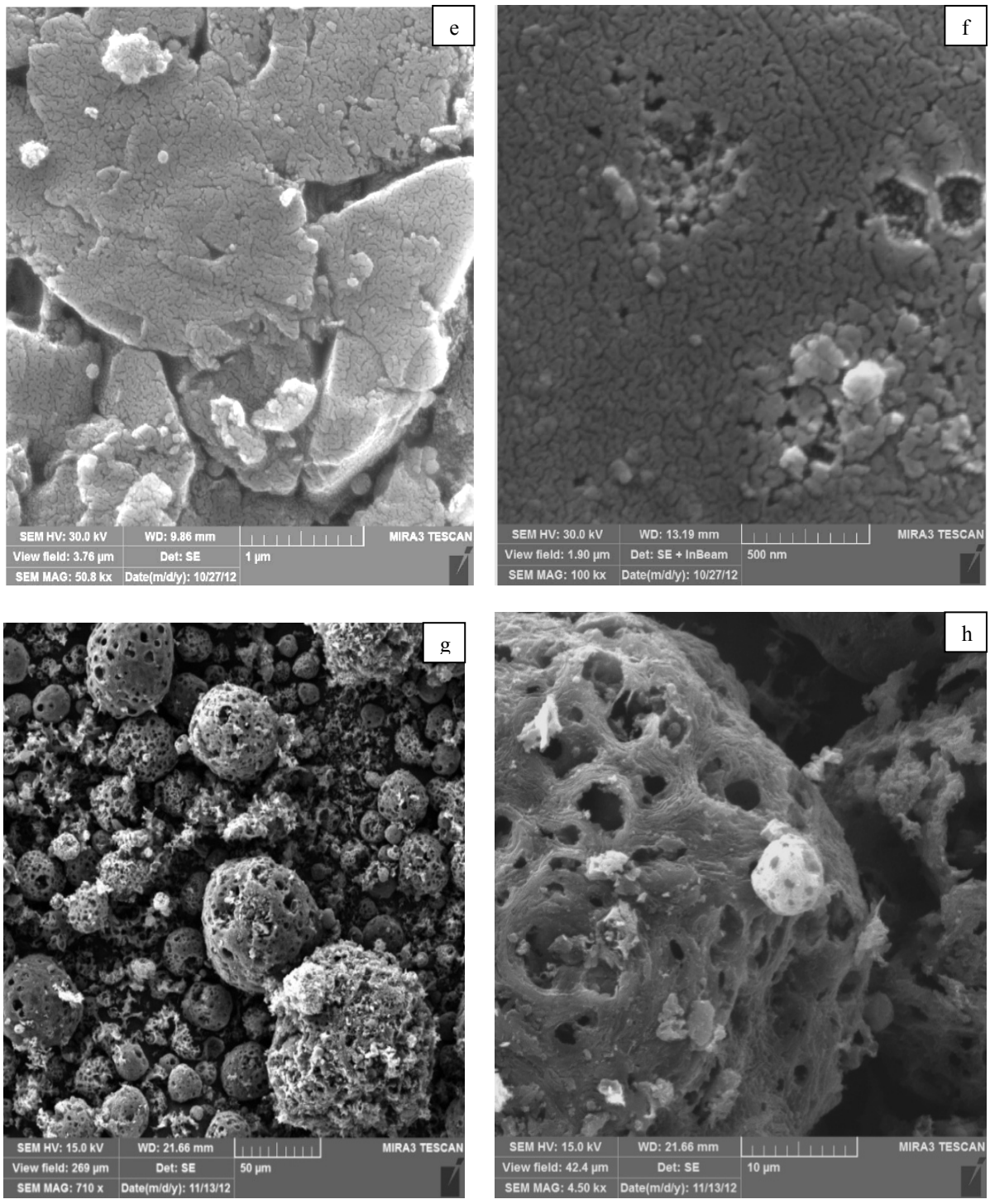


Figure 4-2 : SEM image of AC (e, f) and FA (g, h)

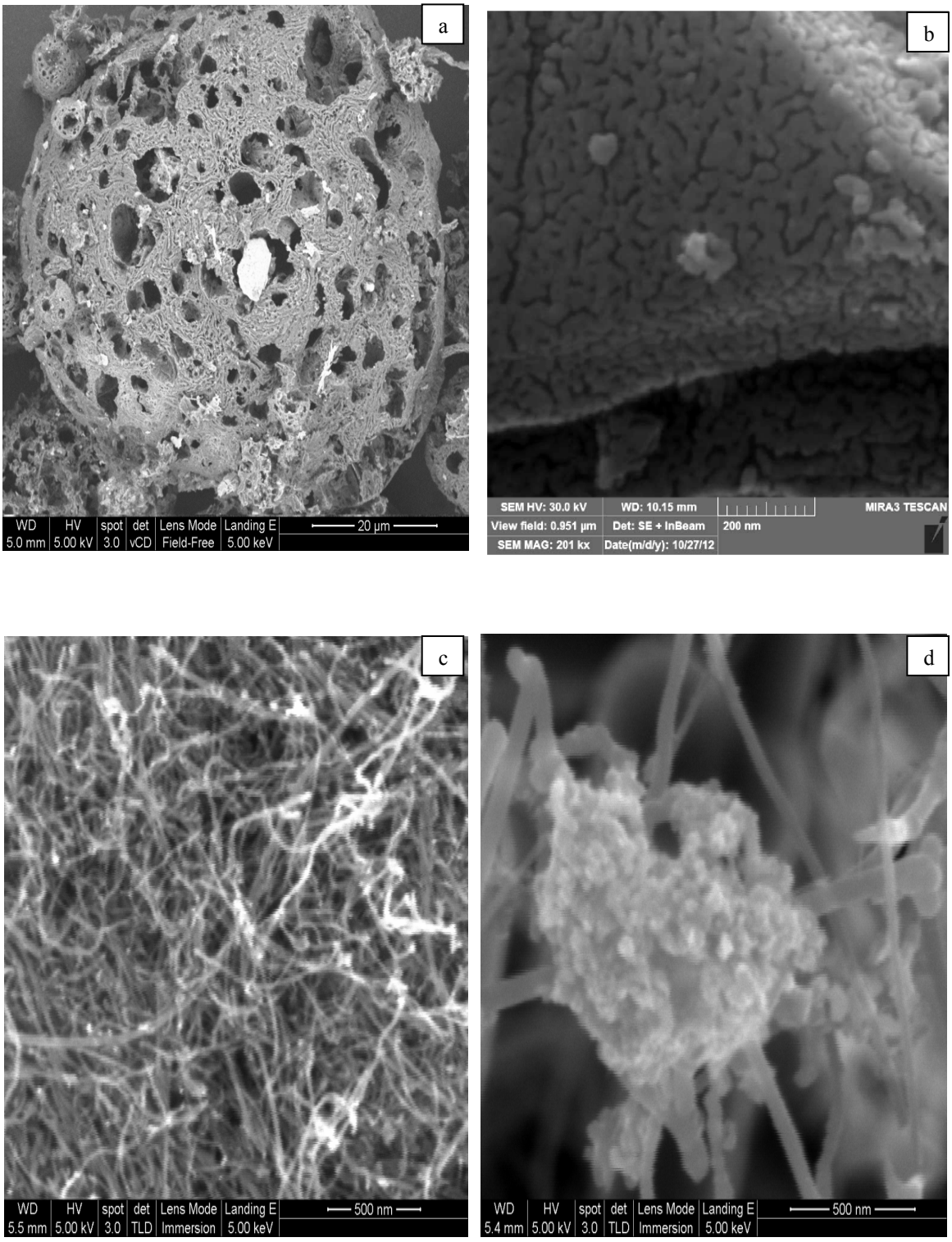
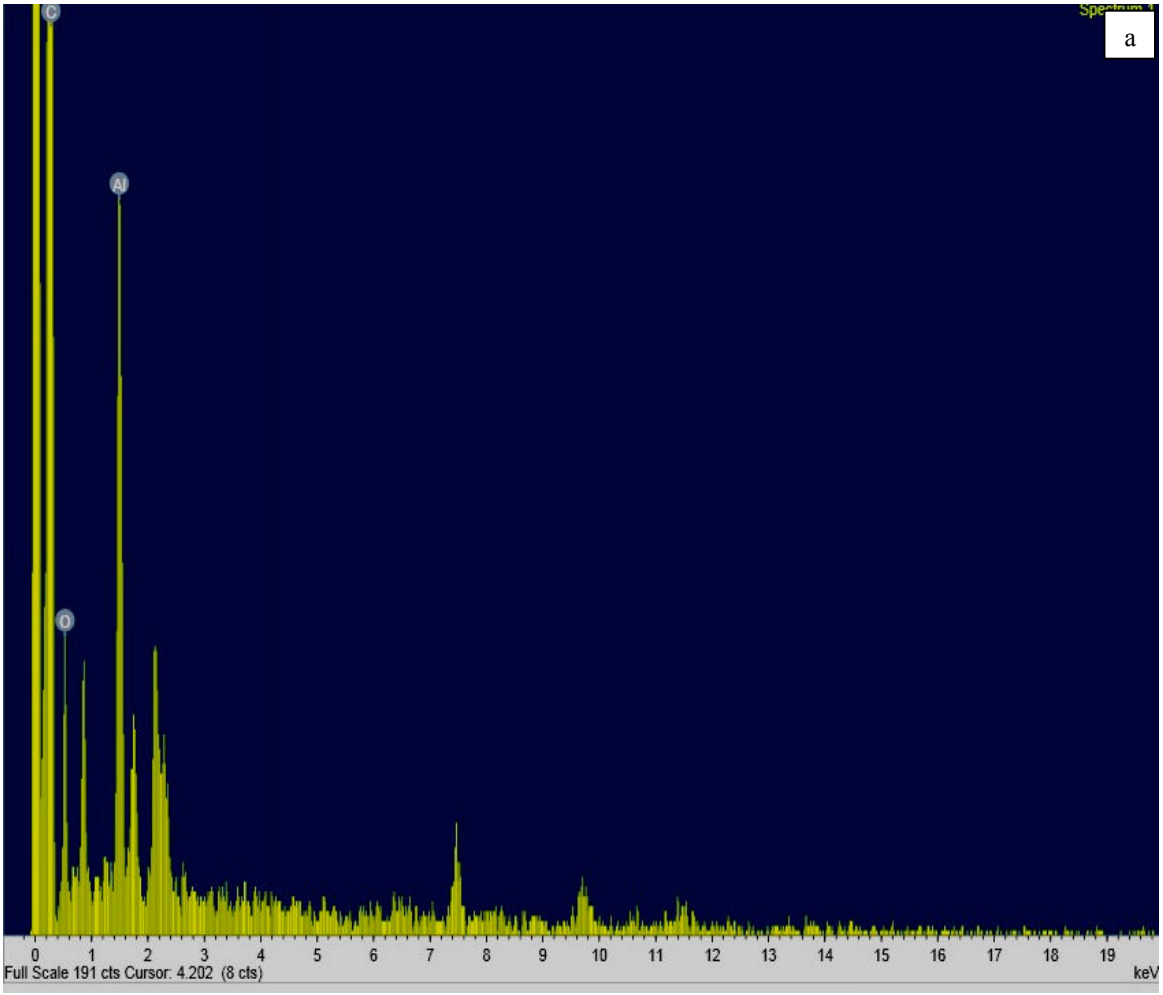
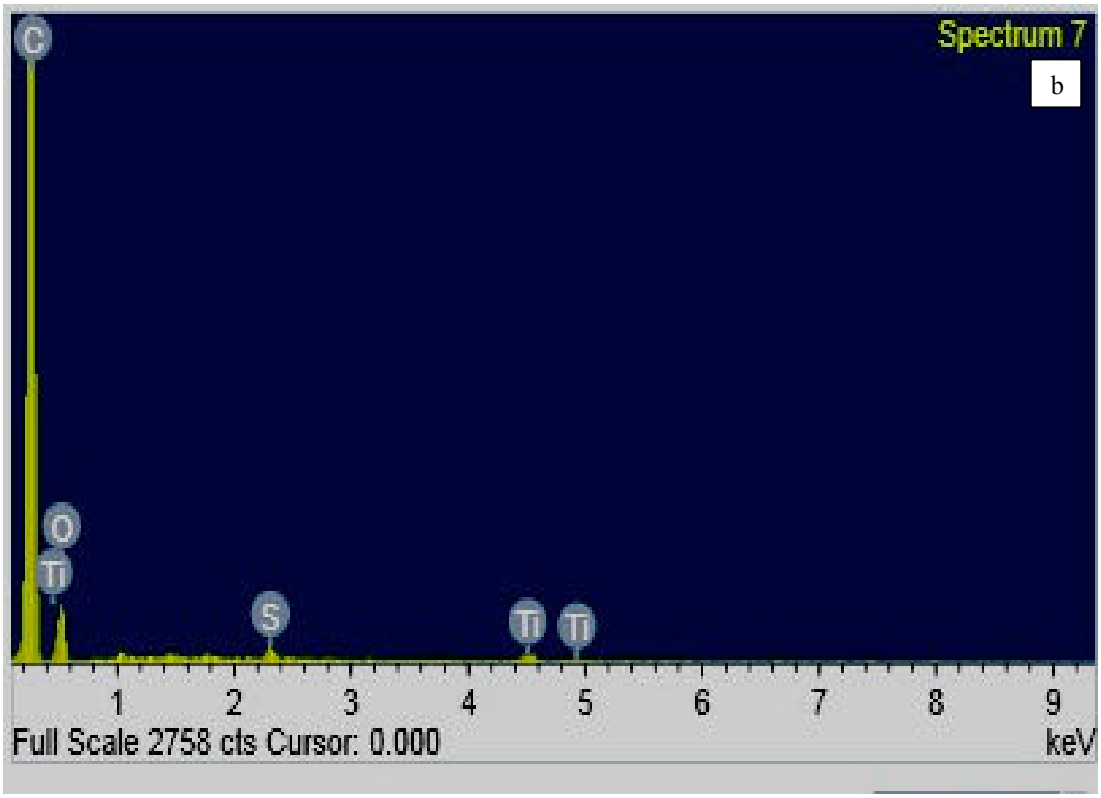


Figure 4-3 : SEM image of (a)FA-Al, (b)AC-Al, (c)CNT-Al and (d) CNF-Al

4.1.2 Scanning Energy Dispersive X-ray Spectroscopy (EDS).

The EDS analyses of the component on the modified adsorbents were obtained for all modified sample by different adsorbents to confirm the impregnation of metals on the adsorbents. The EDS analysis was obtained to the modified AC and CNT, due to their high removal efficiency when compared with both FA and CNF. The spectrums of EDX technique approved the presence of Al, Ti and Fe on the AC, respectively as shown in Figure 4-4 (a, b, c), while Figure 4-5(d, e, f) shows the presence of Al, Ti and Fe on the CNT, respectively.





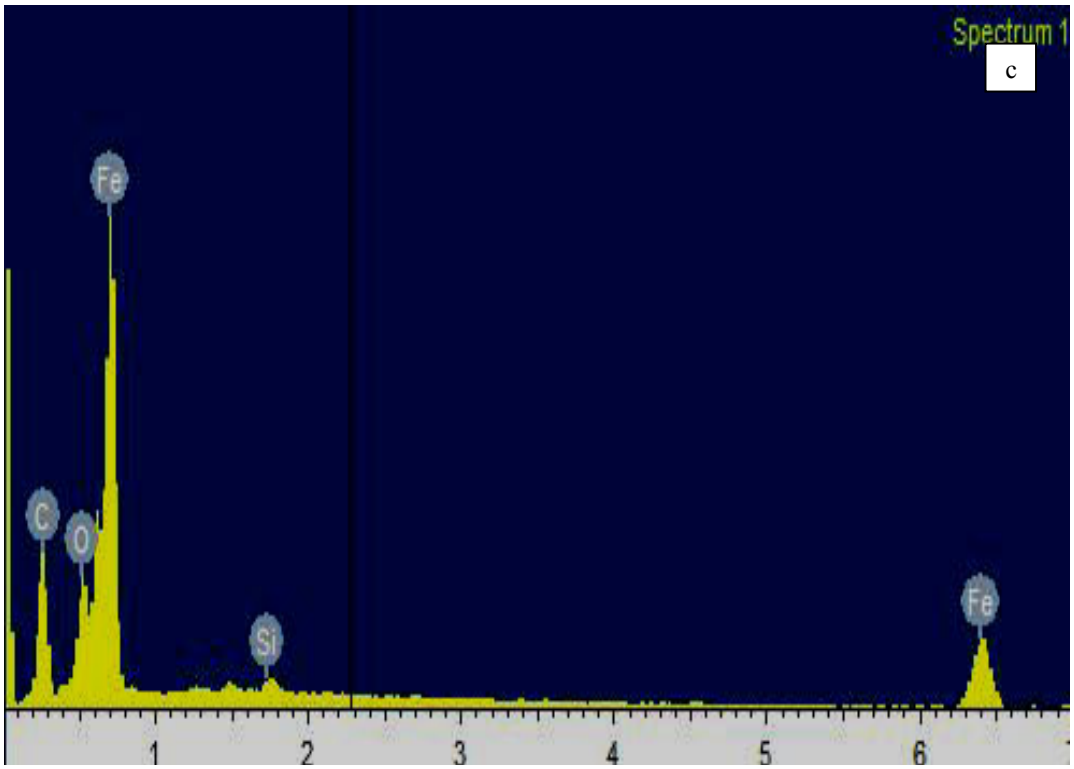


Figure 4-4 : EDS analysis for AC impregnated by (a) Al (b) Ti (c) Fe

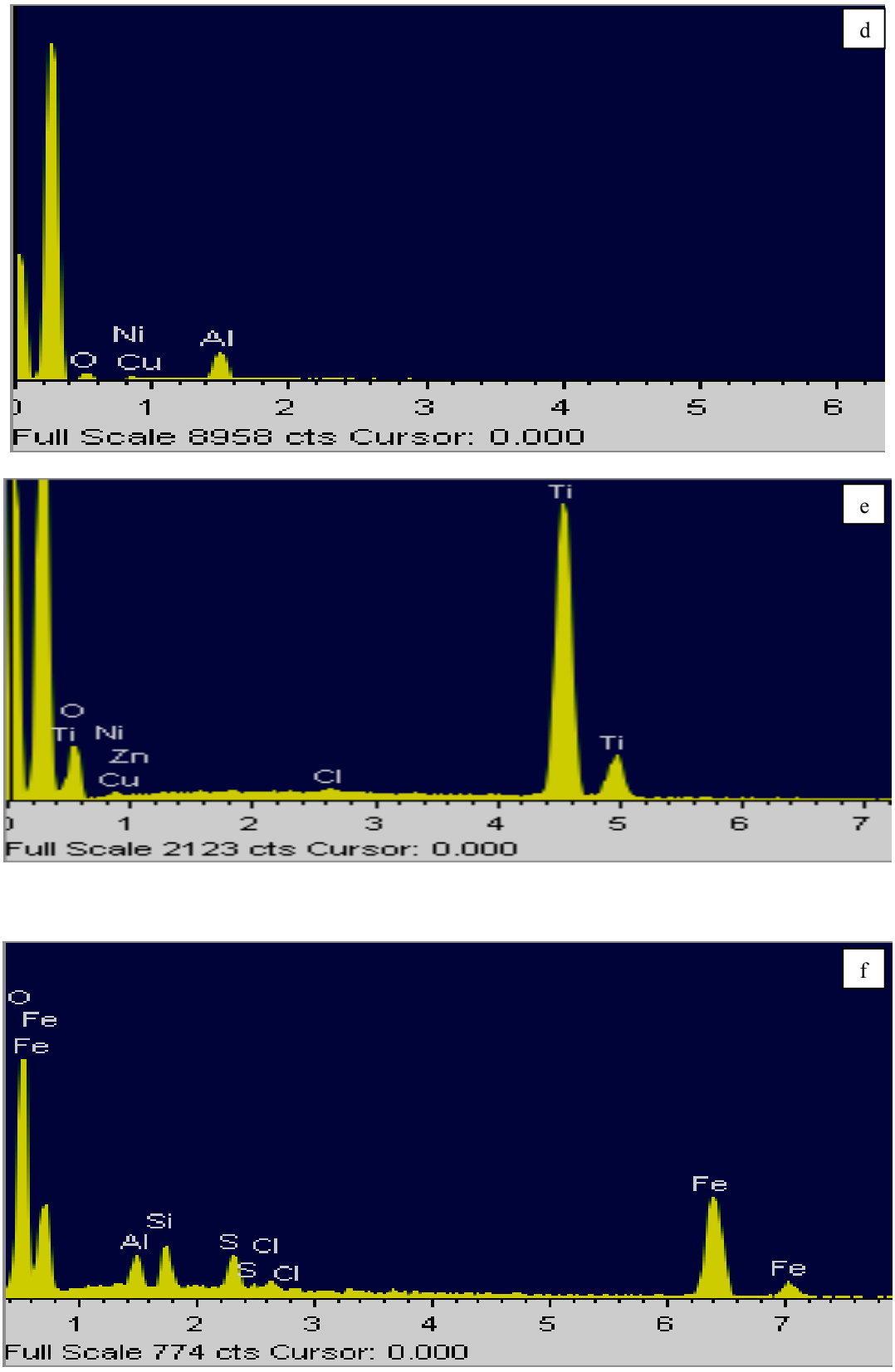


Figure 4-5 : EDS analysis for CNT impregnated by (a) Al (b) Ti (c) Fe

4.1.3 Thermal Analysis of Carbonaceous Adsorbents

The Thermogravimetric (TG) and Derivative thermogravimetric (DTG) curves obtained for the four adsorbents at heating rates of 10^{o}C/min are shown in Figure 4-6 (a, b) and Figure 4-7 (c, d). The TG thermgrams were carried out in air and it was noted that there was some residual remains of the samples when it was heated to about 900^{o}C. For CNTs (Figure 4-6 a), the residue appears reddish, which shows that all the CNTs were oxidized leaving only the catalyst. It can be seen that this decomposition process is a single-stage decomposition reaction where the procedural decomposition temperatures are well defined. For CNFs (Figure 4-6 b), two peaks have been observed. This is due to the wide difference in sizes of CNFs. The CNF's with small diameters decompose first while that of the large diameters takes longer time to decompose and appear as a second peak of the thermogram. AC (Figure 4-7 c) apparently contains volatile materials that burn off during the initial heating process, and metal impurities remain after the heating process is completed. The obtained TG thermgrams for the FA indicate that the used FA has three major components: volatile material (25% weight), carbon based material (35% weight) and other material with high temperature resistance including metals and other impurities as shown in (Figure 4-7 d).

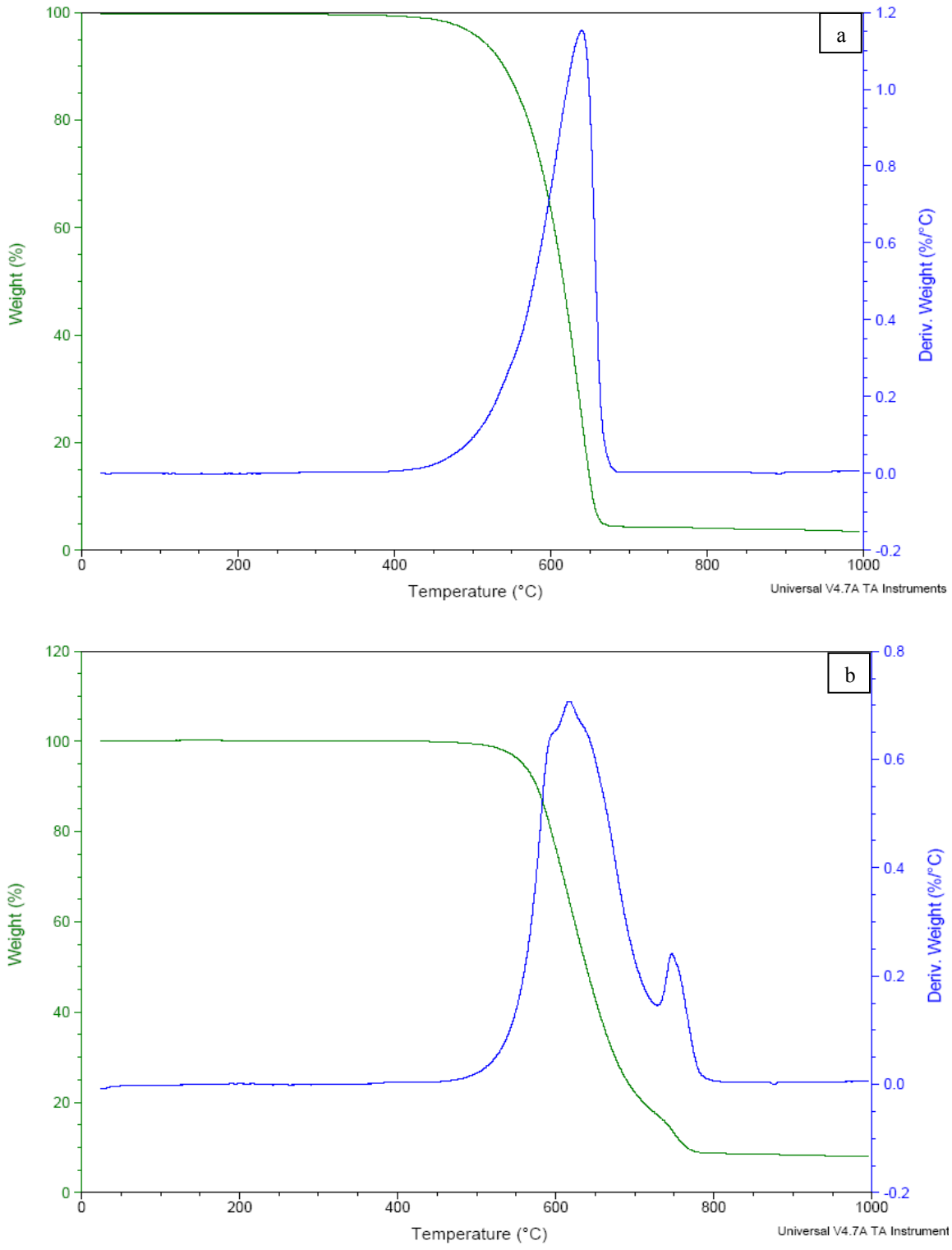


Figure 4-6 : TG curve as green, (DTG) curves as blue colour for (a) CNTs and (b) CNFs

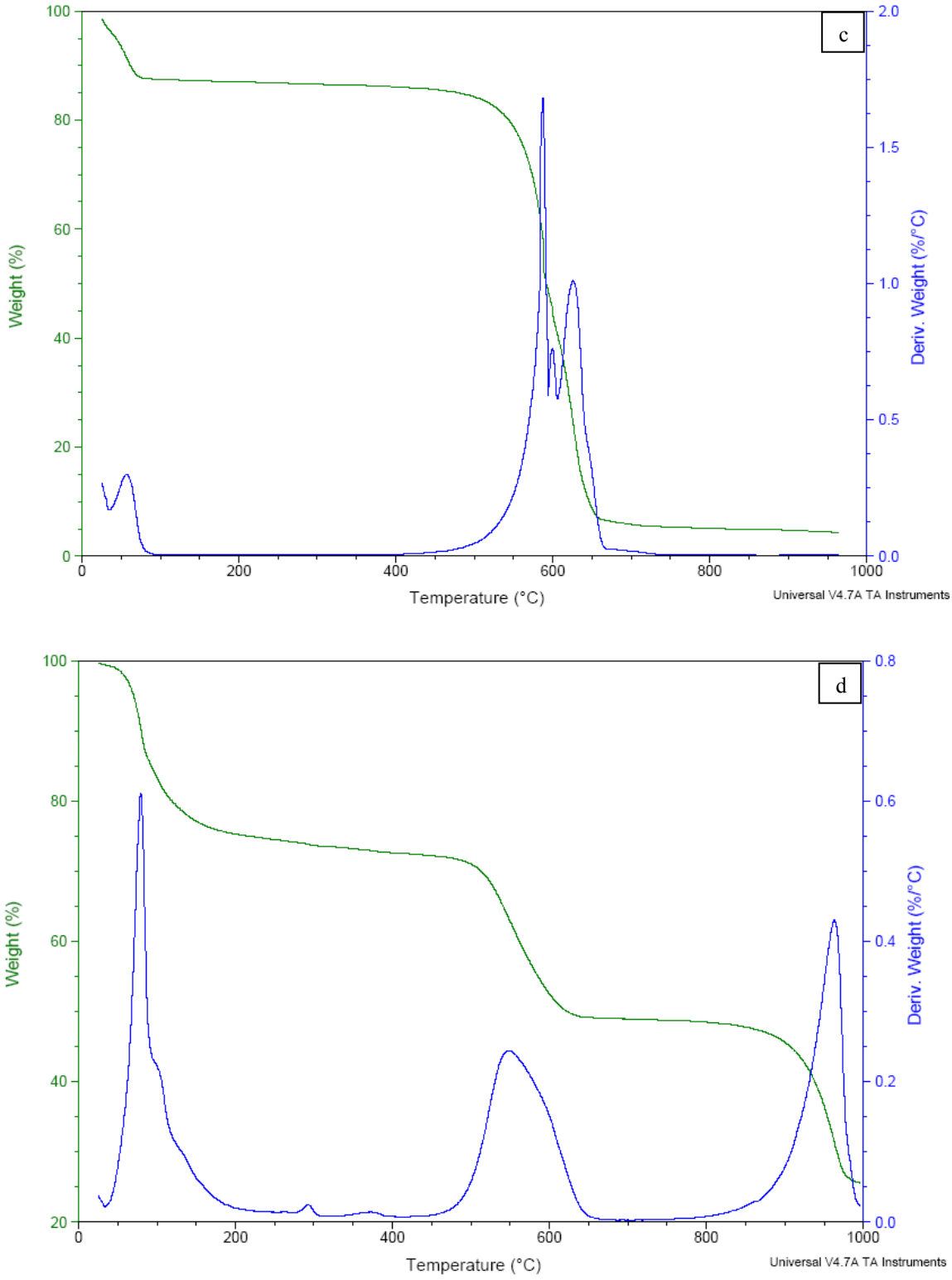


Figure 4-7 : TG curve as green, (DTG) curves as blue colour for (c) AC and (d) FA

4.1.4 BET Analysis

BET surface analysis was performed using Micromeritics ASAP 2020 where fixed mass of carbon of ~0.35 g was degassed initially at 90 ^{o}C for 1 h, flowed by ramping the temperature at 10^{o}C /min to reach 250^{o}C. The sample left at this condition for 5 hours to remove all adsorbed water and air molecules. The mass of the sample was measured again and used for the isotherms. The analysis conditions were performed in the absence of glass rode in order to determine the micorpores surface area. Figures 4-8 illustrate the adsorption-desorption curves of N_2 at 77 K for CNTs, AC, FA and CNFs, respectively. The obtained BET surface area for these carbons as follows: raw CNTs (155.5 m^2/g); raw AC (1126.6 m^2/g); Industrial fly ash (7.1 m^2/g) and raw CNFs (40.7 m^2/g).

Under similar above conditions, the BET surface analysis was obtained for the four modified adsorbents by aluminum as shown in Figure 4-9. The obtained BET surface for the modified adsorbents are as follows: CNT-Al (227.5 m^2/g); AC-Al (1883.7 m^2/g); FA-Al (11.889 m^2/g) and CNF-Al (72.4 m^2/g).

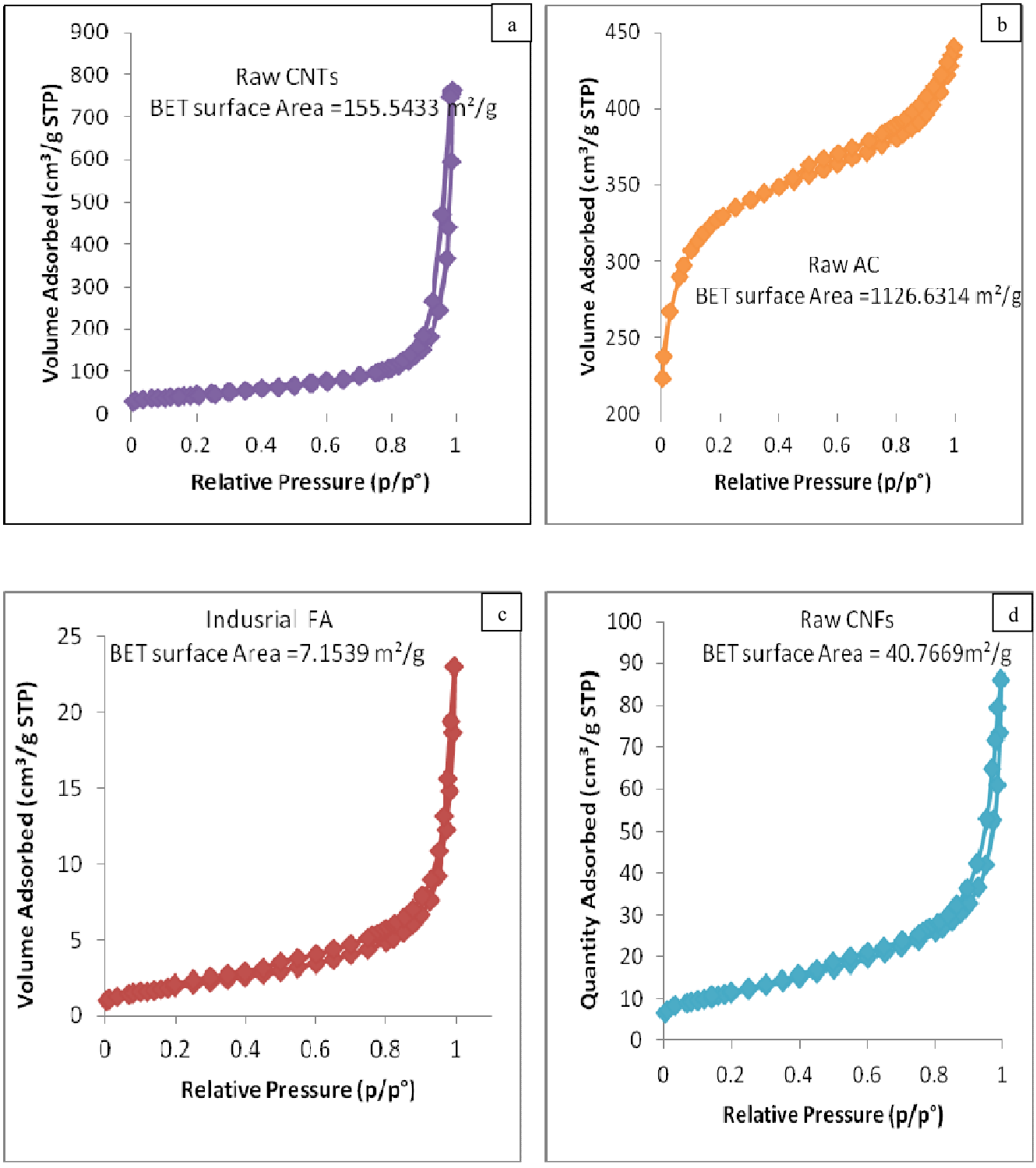
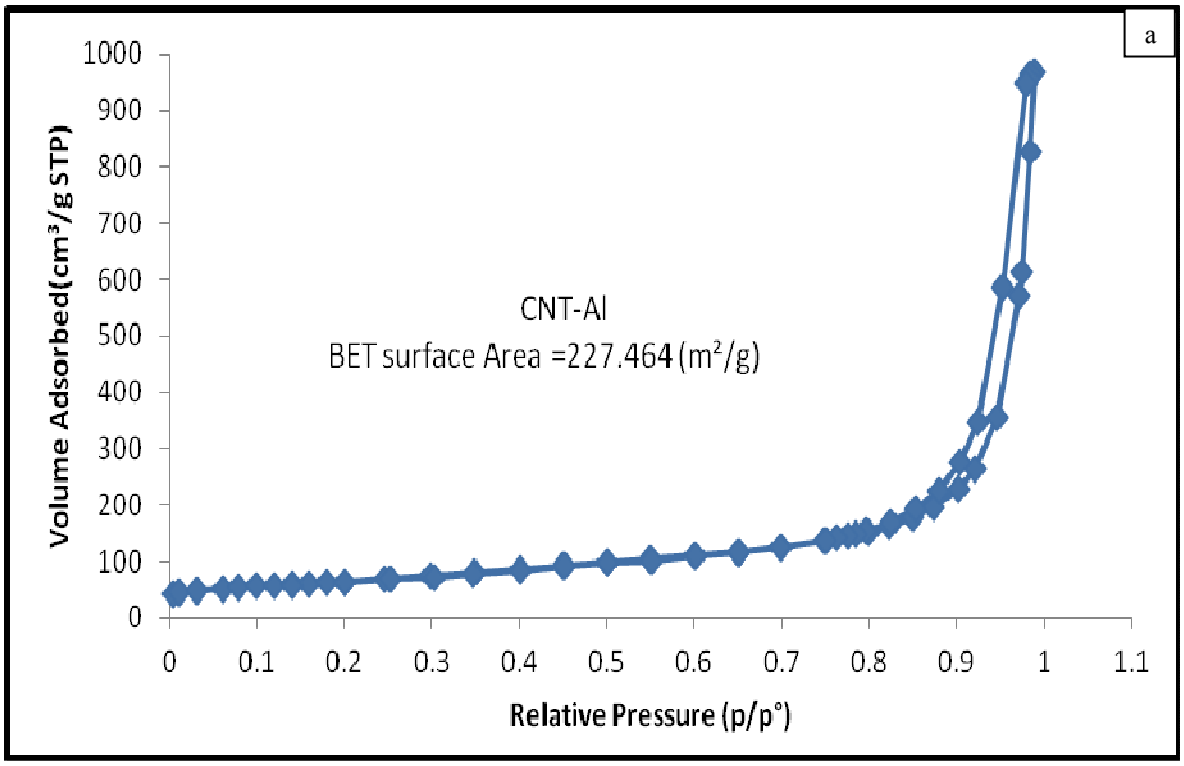
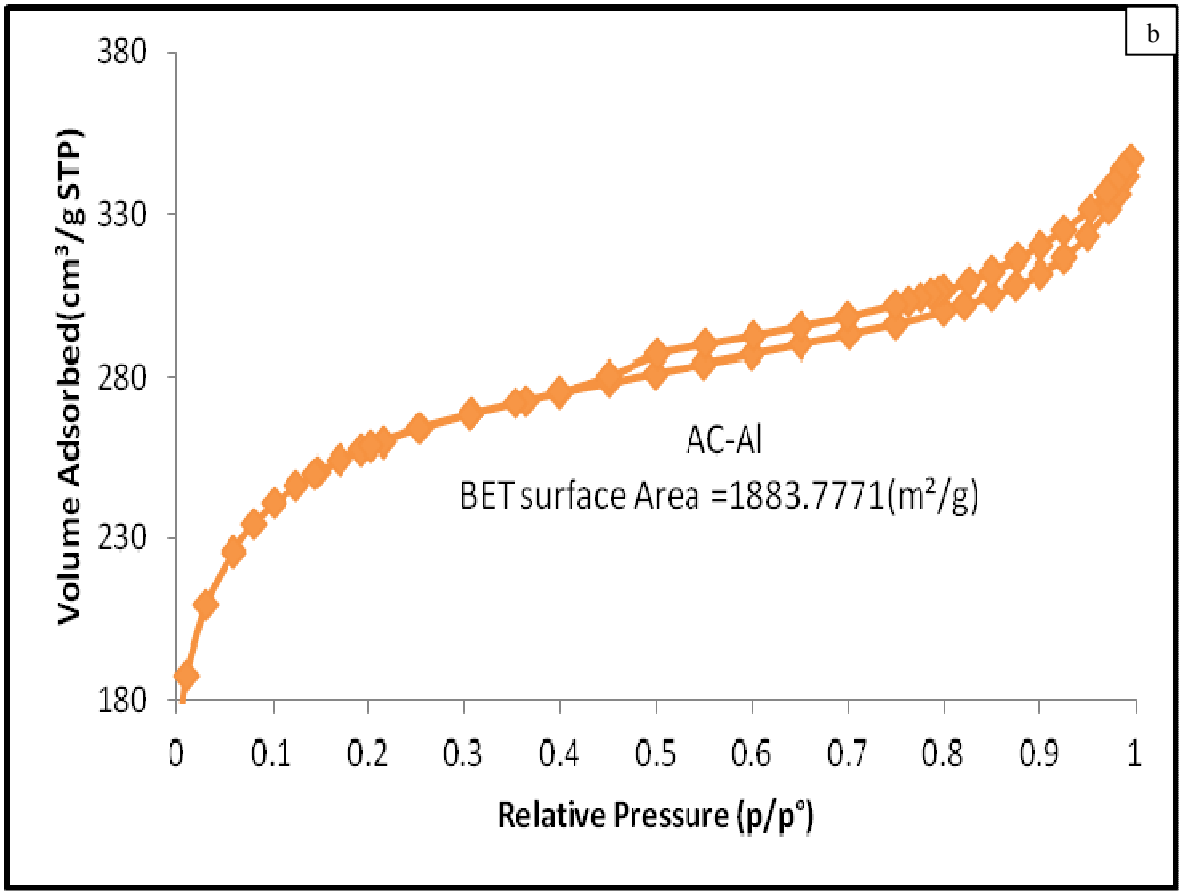
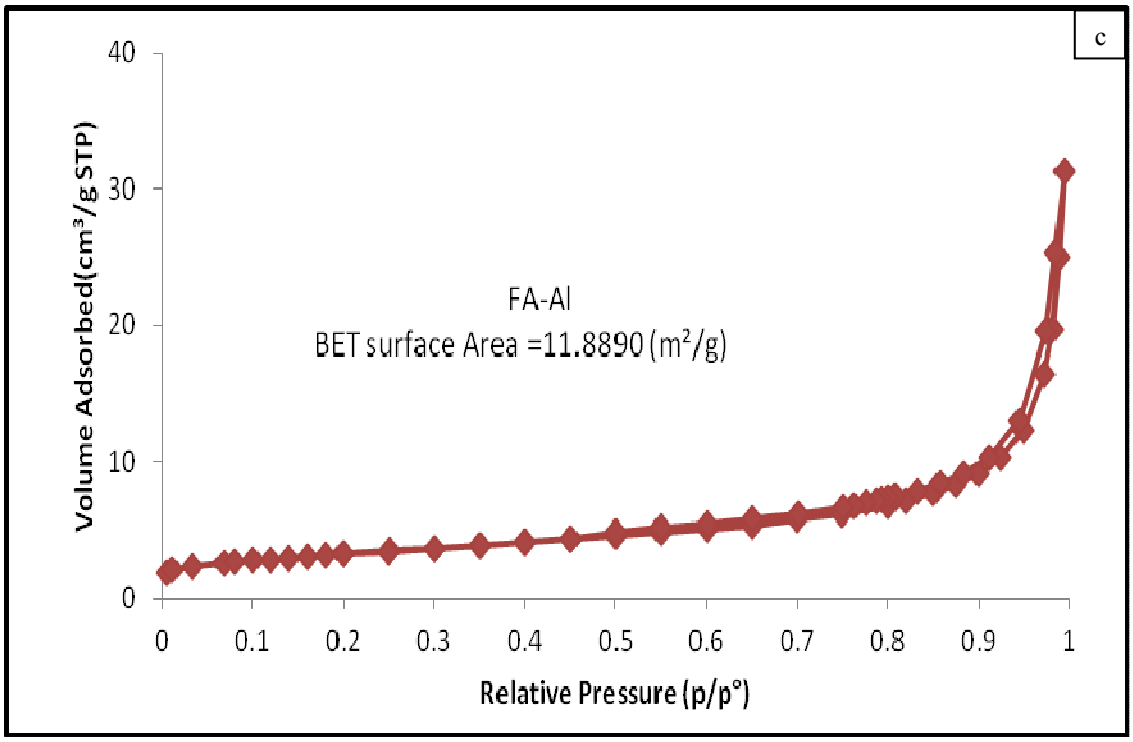


Figure 4-8 : Adsorption-Desorption curves for (a) CNTs (b) AC (c) FA and (d) CNFs


a
1000
900
800
700
600
500
400
300
200
100
0
Volume Adsorbed(cm³/g STP)
CNT-Al
BET surface Area =227.464 (m²/g)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
Relative Pressure (p/p°)


b
380
330
280
230
180
Volume Adsorbed(cm³/g STP)
AC-Al
BET surface Area =1883.7771(m²/g)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Relative Pressure (p/p°)



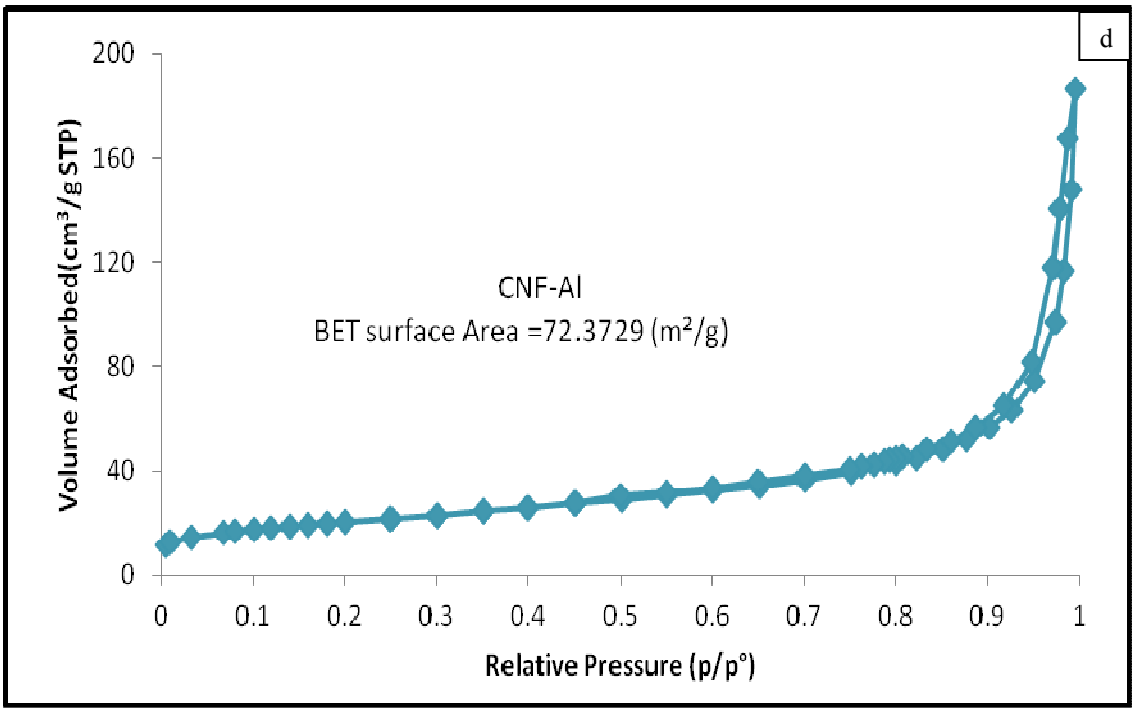


Figure 4-9 : Adsorption-Desorption curves for (a) CNT-Al, (b) AC-Al, (c) FA-Al and (d) CNF-Al

4.2 Removal of Phenol and 4 - Chlorophenol from water

The removal percentage of phenol and 4-chlorophenol from water depends on many parameters such as pH, contact time, agitation speed and the adsorbent dosage, so all these parameters were investigated to obtain the optimum conditions of the removal from water. The percentage removals of phenol and 4-chlorophenol were determined to measure the adsorption capacity for each one.

4.2.1 Removal of Phenol using Carbon Based Adsorbents

The removal of phenol depends on the following parameters:

4.2.1.1 Effect of pH

The removal of phenol by raw and modified carbon based adsorbent with various pH shave been studied. The range of the pH used in the experimental work was in the range of 3 to 9. The following parameters were kept constant namely, contact time of 2 hr, dosage of adsorbent of 50 mg, and shacking speed of 100 rpm. The results obtained by varying the pH on the removal of phenol in water solutions containing AC, CNTs, CNFs and FA adsorbents are shown in Figure 4-10. The pH was found to be a predominant factor affecting the removal of phenol under the studied conditions. It was noticed that with increasing of pH from 3 to 7, the removal of phenol in the solution by all adsorbents increased continuously and then decreased within the pH range of 7-9. It is worth mentioning that the removal was very low for phenol, for all adsorbents, at pH level below 3 and above 7. At pH 7 the maximum percentage removals of phenol, by AC, CNTs, FA and CNFs were found to be approximately 65%, 47%, 43% and 31%, respectively. Overall, the AC and CNTs exhibits a slightly higher removal compared to CNFs and FA. The explanation of the high removal of phenol at neutral region (pH 7) refer to that negatively charged phenolate ions bind through electrostatic attraction to positively charged functional groups on the surface of adsorbents , thus at this pH more functional groups carrying positive charge would be exposed. While in pH above 7.0, it seems that the carbon materials possess more functional groups carrying a net negative charge, which tends to repulse the anions, thus adsorption decrease.

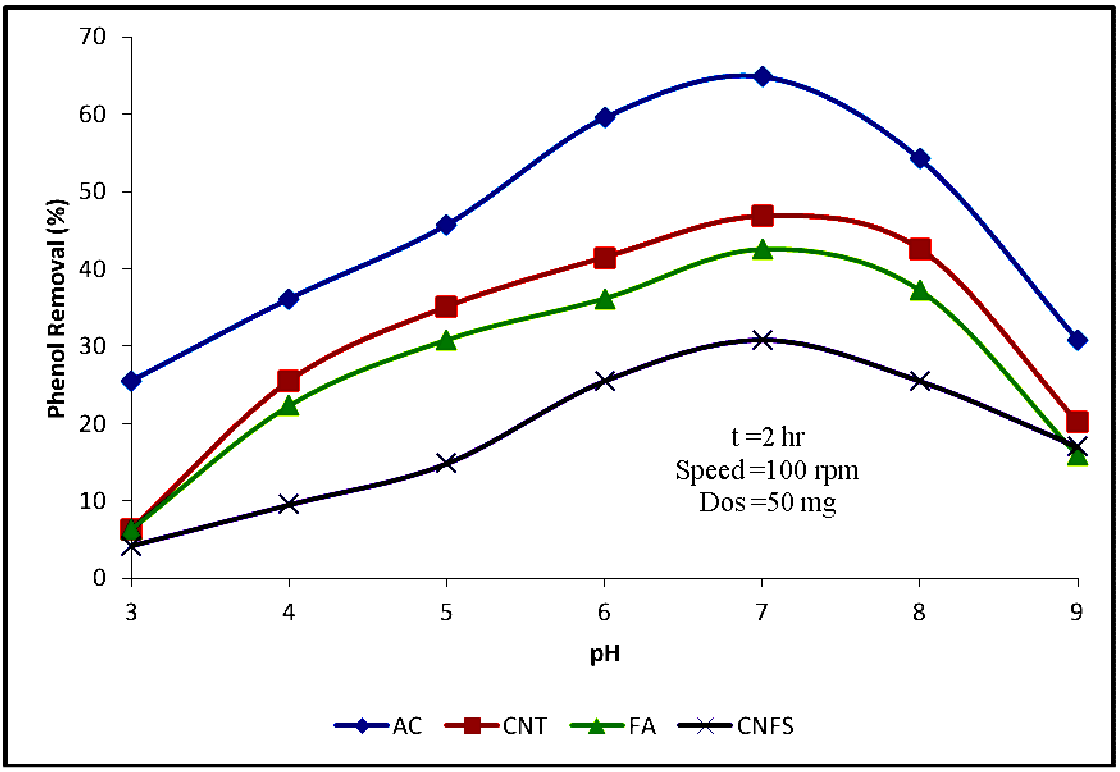


Figure 4-10 : Effect of pH on the phenol removal efficiency by Raw CBAs

In addition, the removal of phenol by the four modified adsorbents with various pHs have been studied and the results are shown in Figures 4-11 to 4-13. The pH used in the experimental work ranges from 3 to 8 and the data from Figure 4.10 was introduced to show the comparison between the raw and modified adsorbents on the removal efficiency of phenol. Similar phenomena of the effect of pH on the removal were observed for all modified adsorbent. It was noticed that with the increase in pH from 3 to 8, the removal of phenol by all modified adsorbent was enhanced. At pH 7, the maximum percentage removals of phenol, by AC-Al, AC-Fe and AC-Ti were achieved and found to be approximately 85.3%, 84.2 % and 83%, respectively as seen from Figure 4-11. In contrast, at pH 7, the removal by CNT-Al, CNT-Fe and CNT-Ti as shown in Figure 4-12 was found to be 76.4%, 74% and 73%, respectively. The same phenomena were recognized for the removal by FA-Al, FA-Fe and FA – Ti at pH7 as shown in Figure 4.13. The removal of phenol by CNFs-Al, CNFs-Fe and CNFs-Ti is found to be around 75%, 72% and 70%, respectively as shown in Figure 4-14.

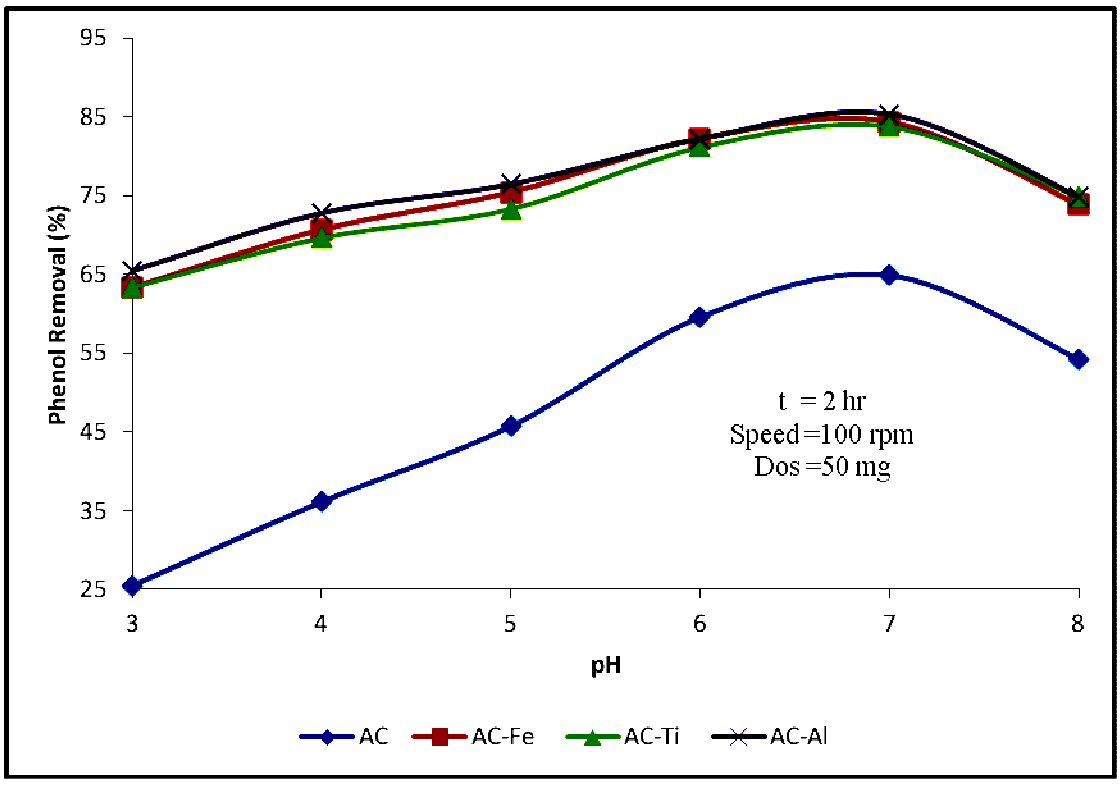


Figure 4-11 : Effect of pH on the phenol removal efficiency by raw and MAC

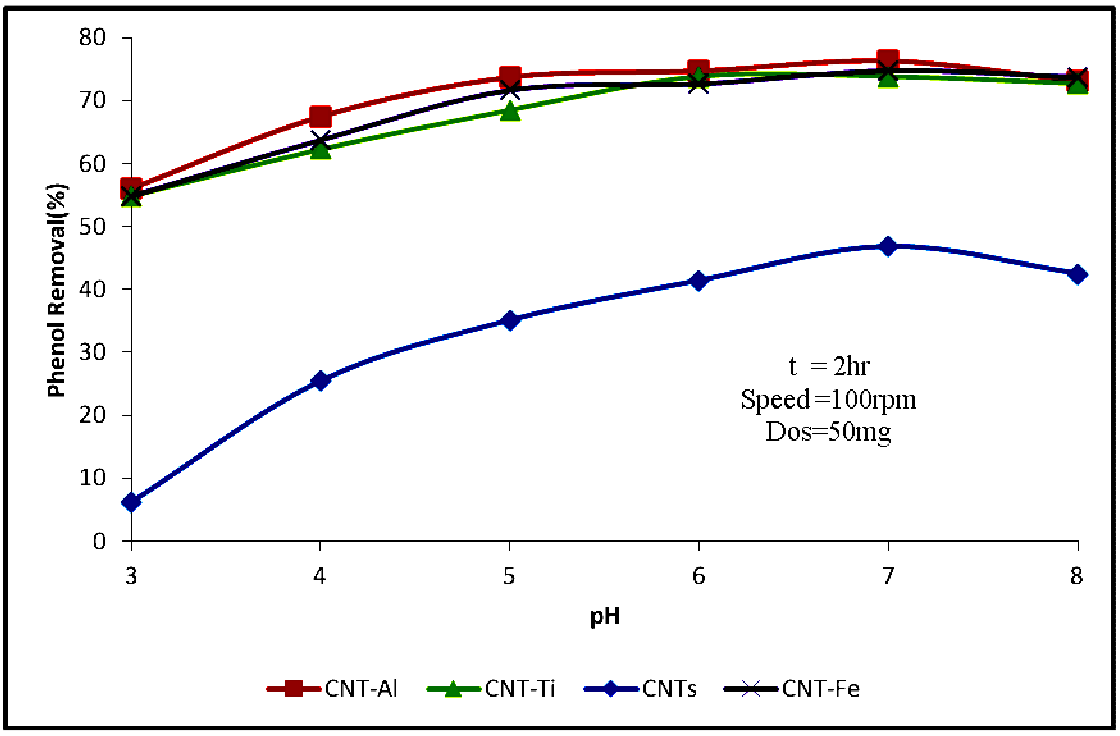


Figure 4-12 : Effect of pH on the phenol removal efficiency by raw and M CNTs

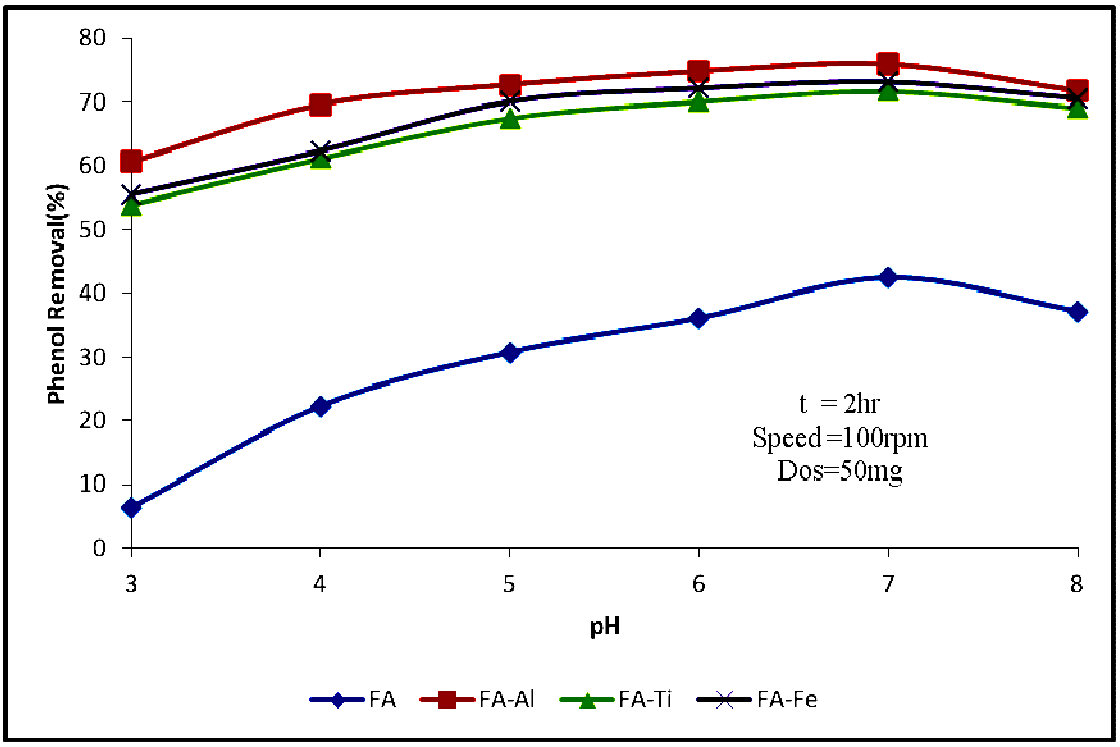


Figure 4-13 : Effect of pH on the phenol removal efficiency by raw and MFA

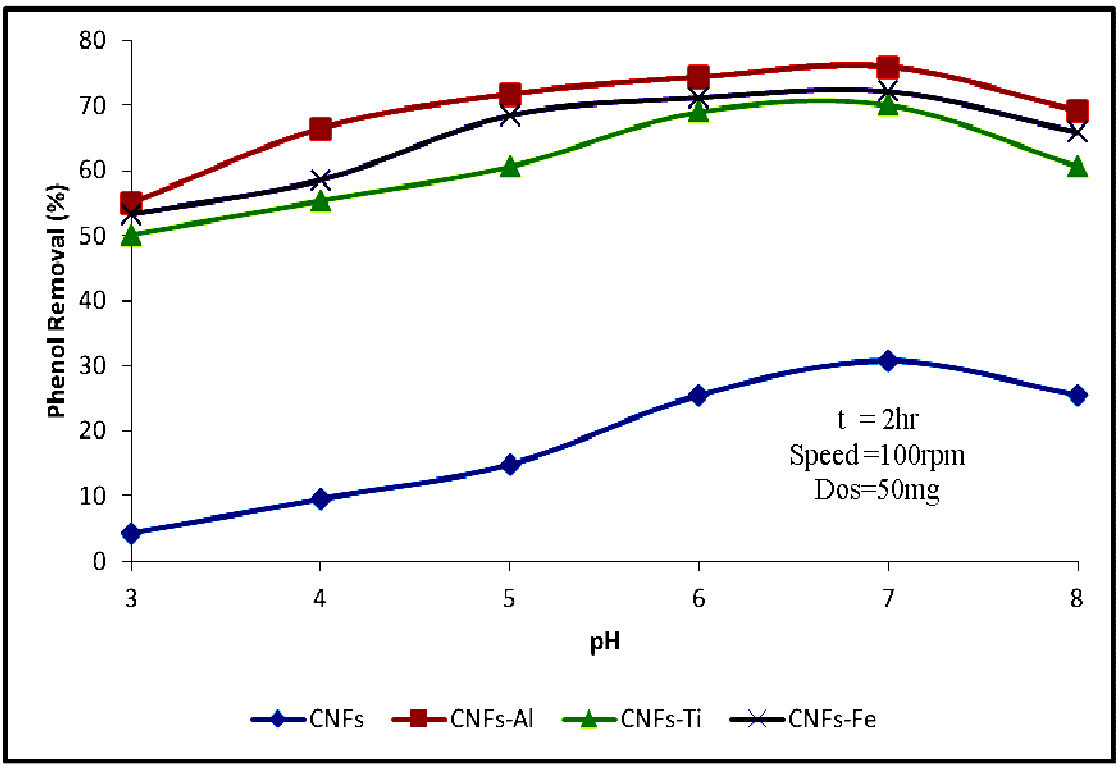


Figure 4-14 : Effect of pH on the phenol removal efficiency by raw and MCNFs

Figure 4-10 shows the removal percentage of phenol from water as a function of pH by the four based adsorbents in their regular forms. The impregnations of Al, Fe and Ti on these four adsorbents lead to increase in the removal of phenol significantly. The removal of phenol by raw AC reach to 65% as in Figure 4.10 at pH7 compared to 85.3% by using AC-Al as shown in Figure 4-11, making 20% increasing. Similar phenomena were observed when the Al was impregnated in to CNT, FA and CNFs. The removal percentage increased by 29%, 32% and 44%, respectively. This result indicate that the weak adsorbent (CNFs) has highest affection by the impregnations of Al on its surface than the strong adsorbent AC on the removal process.

Similar results were noticed when CBAs were impregnated by Ti and Fe. Cleared improvement in the removal of phenol was observed. In fact, the impregnations of metals lead to production of hydroxide ions on the surface of the adsorbents which increases the adsorption ability of contaminants (phenol) [87]. The surface chemistry of the adsorbents can modified by chemical impregnation (Al_2O_3, TiO_2, Fe_2O_3) which lead to high increase on the adsorption capacity of the adsorbents [88].

4.2.1.2 Effect of contact time

By keeping the pH, agitation speed, adsorbent dosage at constant values, it was observed that phenol adsorption has positive results in term of time in the first two hours. The amount of phenol adsorbed in the raw carbon based adsorbents as in Figure 4.15 increased rabidly during the first 2 hours. Subsequently, after 2 hours the removal starts decreasing with increasing in time, making very short time of the equilibrium state. The decreasing in the removal indicate that the phenol start desorption from the adsorbents surfaces. The best explanation of this desorption, is that all the adsorbents reach saturation state after two hours and the phenol molecules that not attached strongly with the adsorbents surface able to escape back to the bulk solution especially under high agitation speed 100 rpm. The same phenomena was observed by using modified AC, CNTs, FA and CNFs as shown in Figures 4-16 to 4-19, respectively.

From these results, it was found that the modified carbon based adsorbents has high adsorption efficiency to phenol and the optimum time to reach maximum removal was found to be 2 hours.

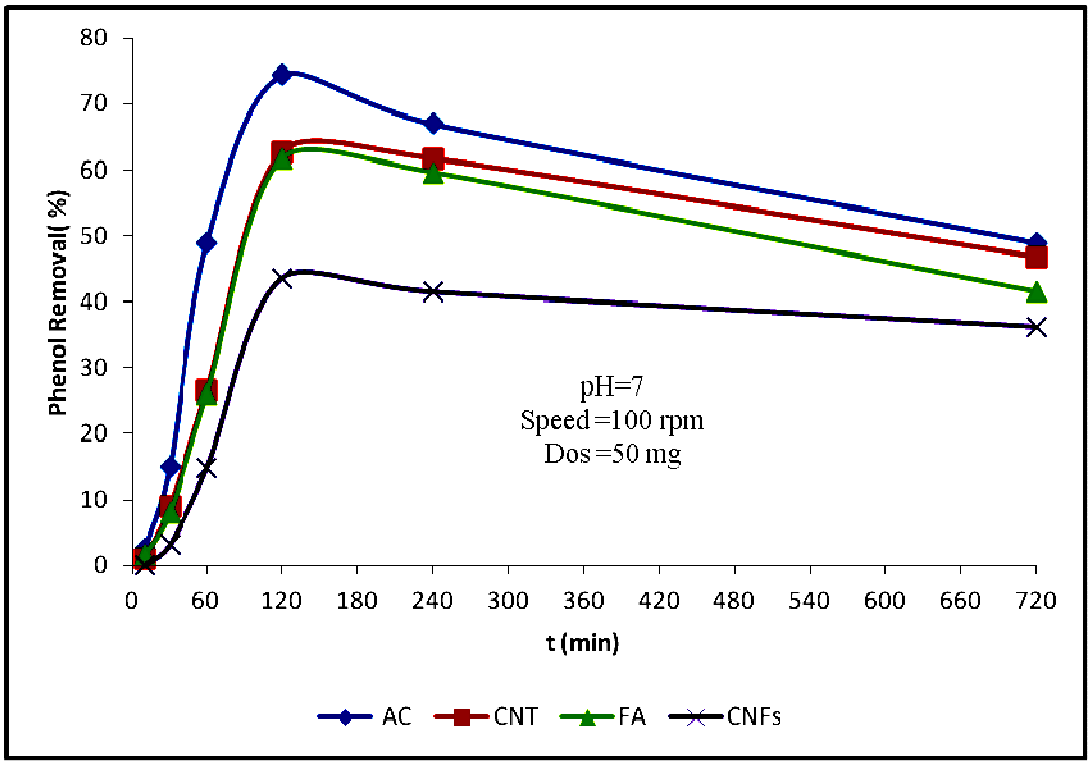


Figure 4-15 : Effect of contact time on the phenol removal efficiency by raw CBAs

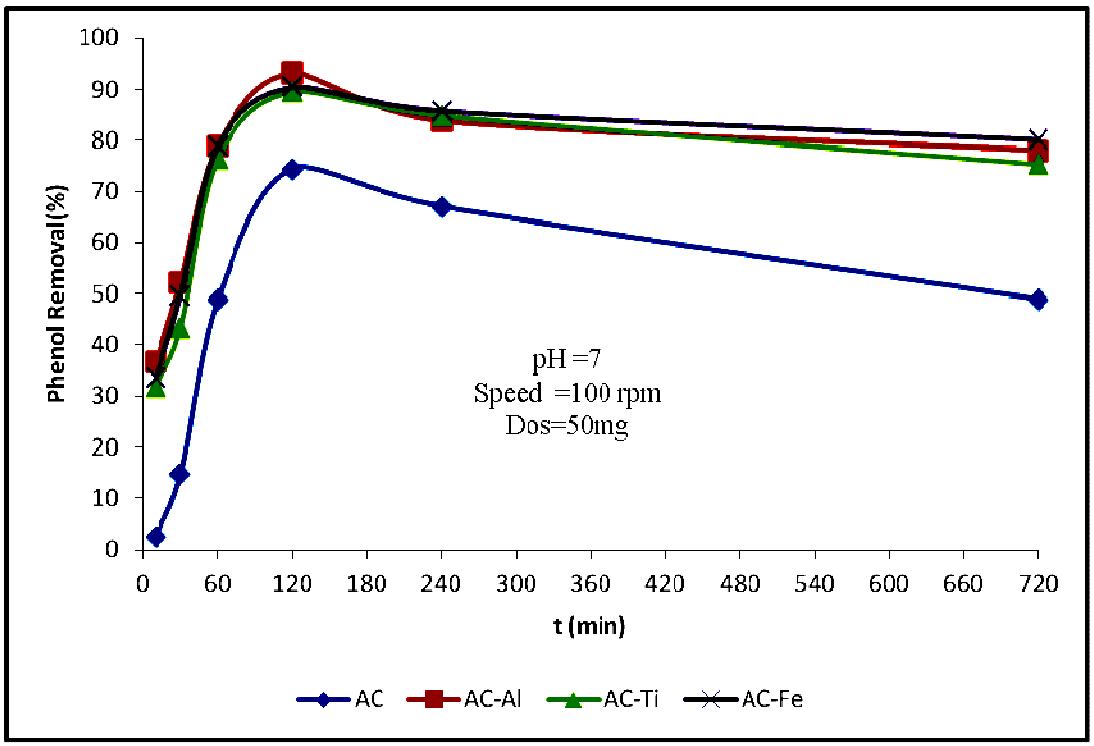


Figure 4-16 : Effect of contact time on the phenol removal efficiency by raw and MAC

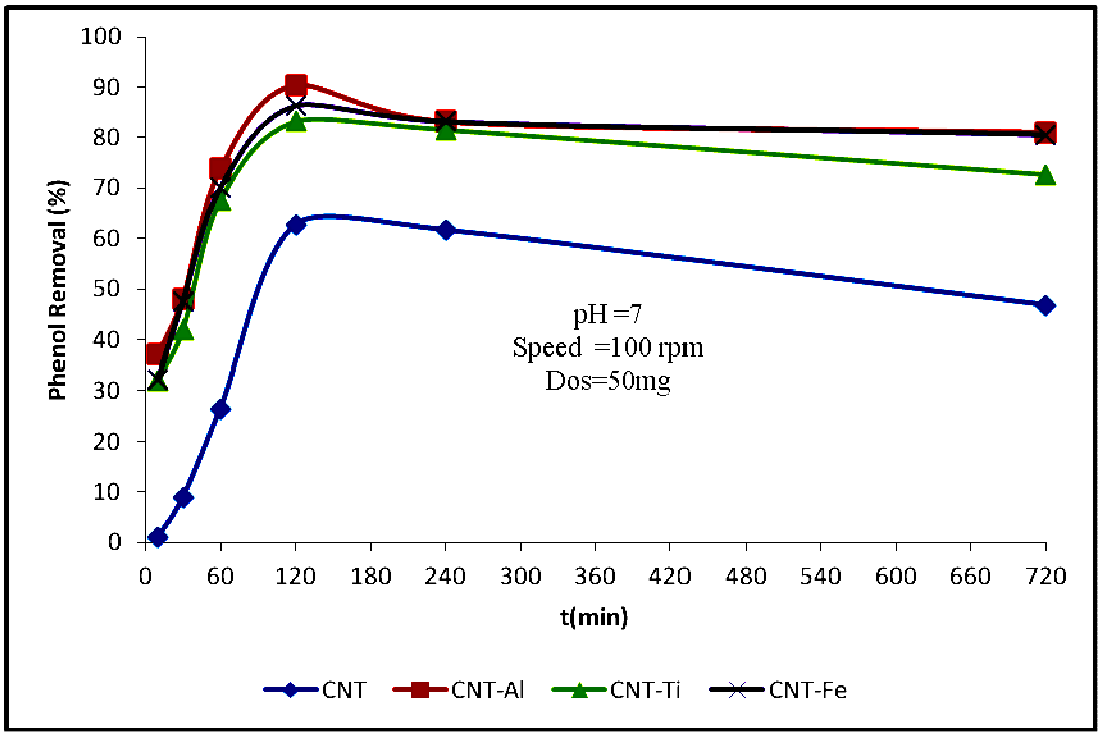


Figure 4-17 : Effect of contact time on the phenol removal efficiency by raw and MCNTs

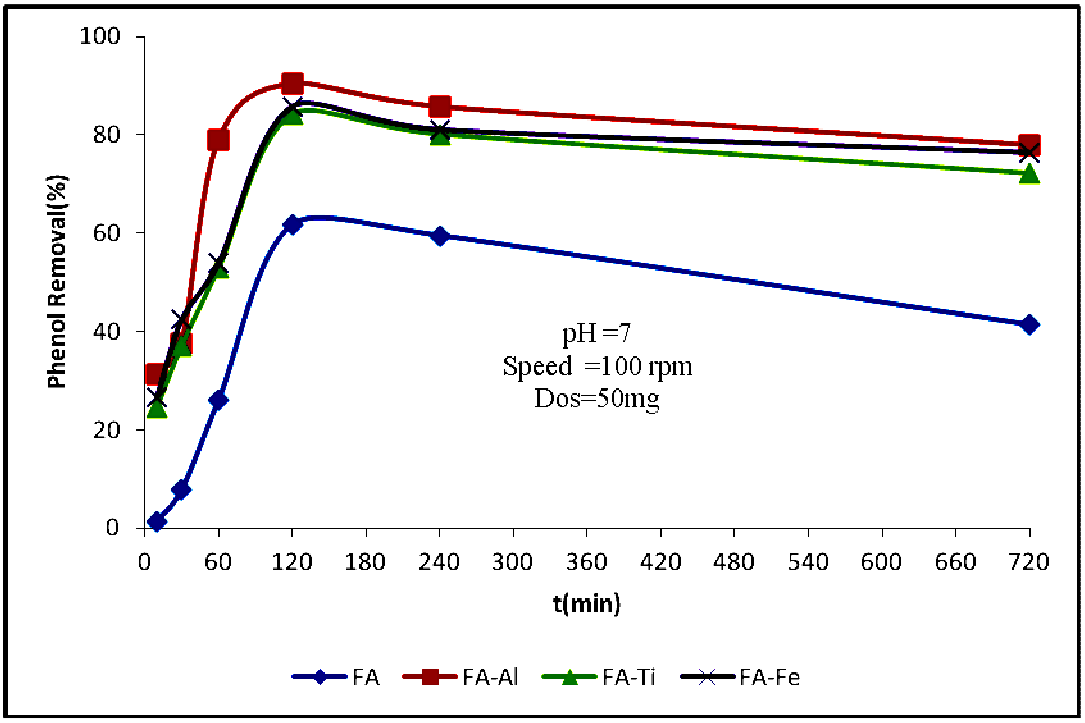


Figure 4-18 : Effect of contact time on the phenol removal efficiency by raw and MFA

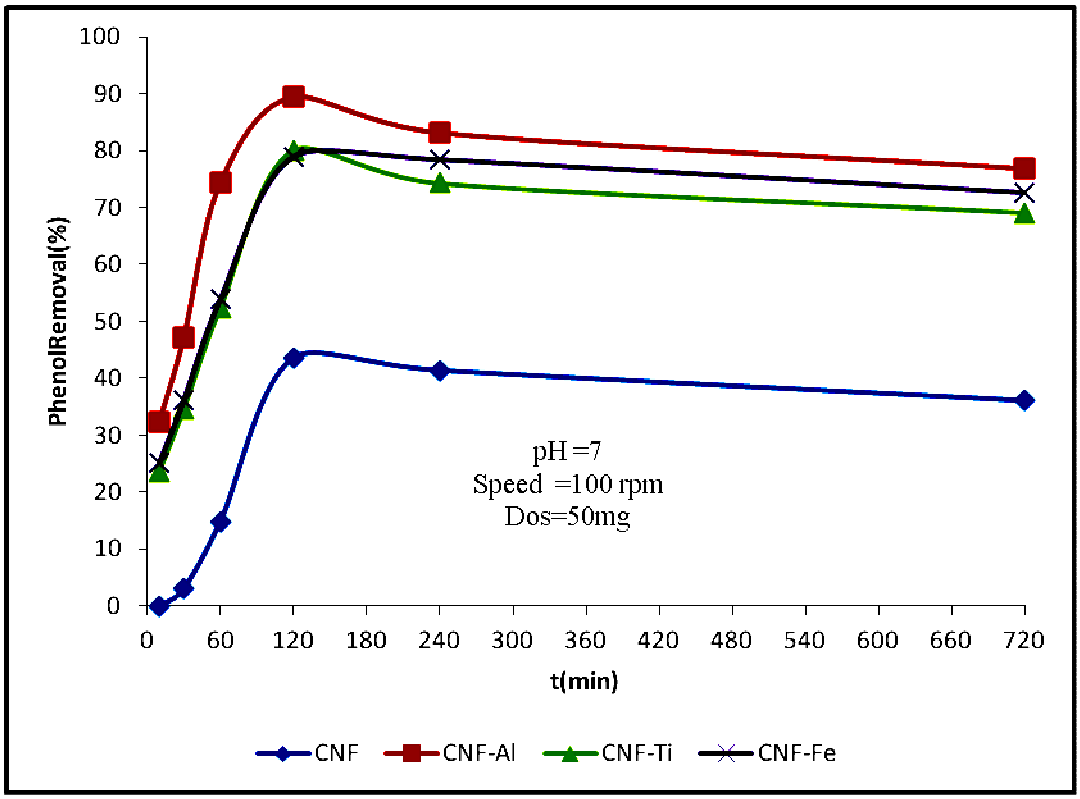


Figure 4-19 : Effect of contact time on the phenol removal efficiency by raw and MCNFs

4.2.1.3 Effect of Agitation speed

The peak removal at pH7 and 2 hours of contact time was used to study the effect of the agitation speed on the adsorption capacity of the phenol by raw carbon based adsorbent by varying the agitation speed from 50 to 250 rpm as shown in Figure 4-20. It has been observed that the percentage of removal increased slightly by increasing the agitation speed until it reachs the maximum at150 for AC and CNT and at 200 rpm for CNF and FA at 200 rpm. This phenomena related to the fact that the increasing in the agitation speed under fixed other parameters, enhances the diffusion of the phenol molecular towards the surface of the adsorbents and decreasing the mass transfer resistance when the agitation increases. This situation leads to offer external mass transfer rate of phenol and thus give more adsorption capacity. From Figure 4-20, it can be concluded that the contact between solid and liquid is more effective at (150-200 rpm) for phenol removal under the removal condition stated in this work. So, we fixed the speed at 200 rpm as optimum agitation speed.

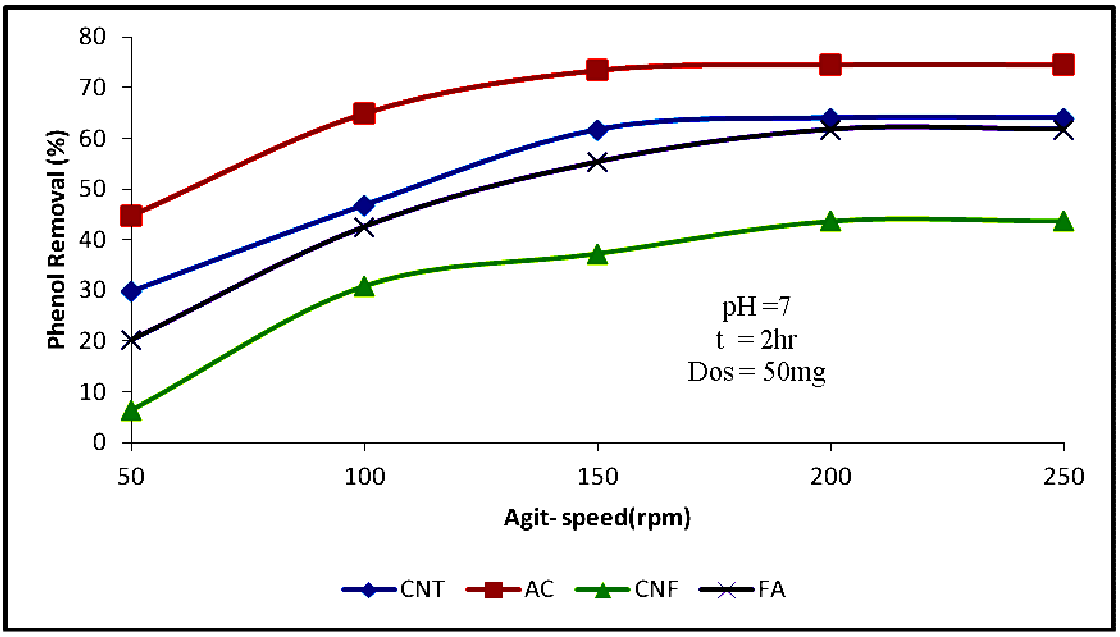


Figure 4-20 : Effect of agitation speed on phenol removal efficiency by Raw CBAs

Similarly, the peak removal at 2 hours contact time and the pH7 used to study the effect of the agitation speed on the adsorption capacity of the phenol by modified adsorbents as shown in Figure 4-21 to 4-24. It has been observed that the percentage of removal increased with increasing speed up to 150 rpm for all modified adsorbents. Then, the removal remains constant with the increasment in the agitation speed. By comparing the raw adsorbents in Figure 4-20 and modified adsorbents in Figures 4-21 to 4-24 on the adsorption mechanism of phenol, it can be seen that the removal is clearly increasing due to the impregnation of ions on the adsorbents. The aluminum ion showed better results than the titanium and iron. From the Figure 4-20 to 4-24, it can be concluded that the contact between solid and liquid is more effective at 150 rpm for all adsorbent except for raw AC, FA and CNFs (200 rpm) for phenol removal under the removal condition stated in this work for all the modified adsorbents. Due to that, all experiments have been done in one batch and we fixed the agitation for optimum phenol removal at 200 rpm for all experiments.

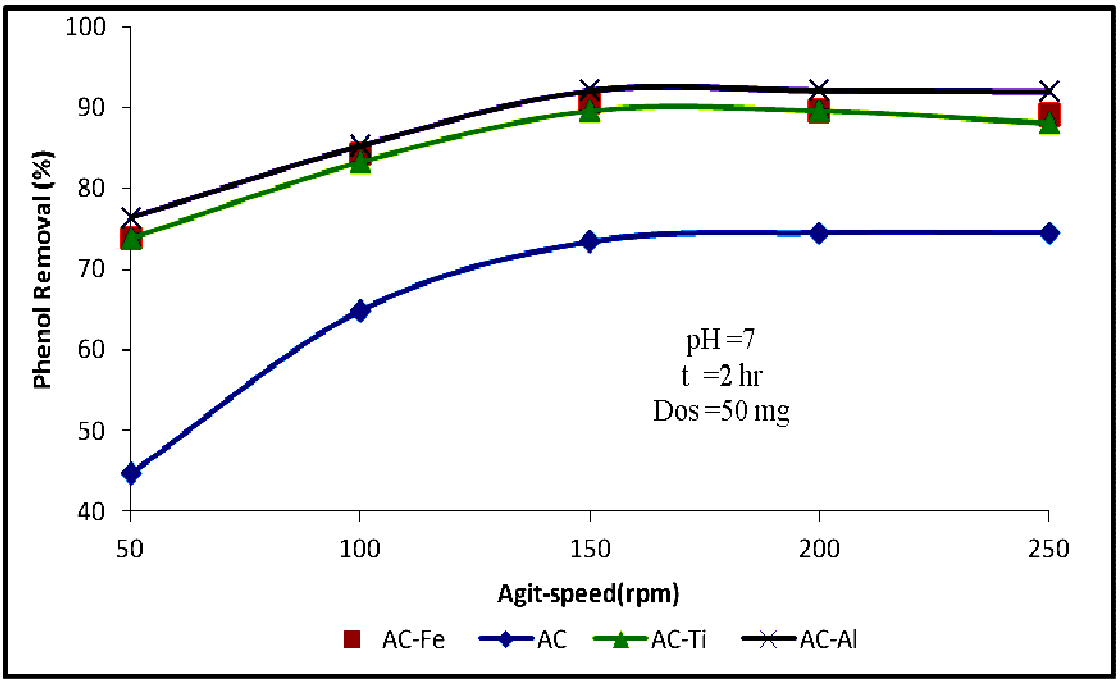


Figure 4-21 : Effect of agitation speed on phenol removal efficiency by raw and MAC

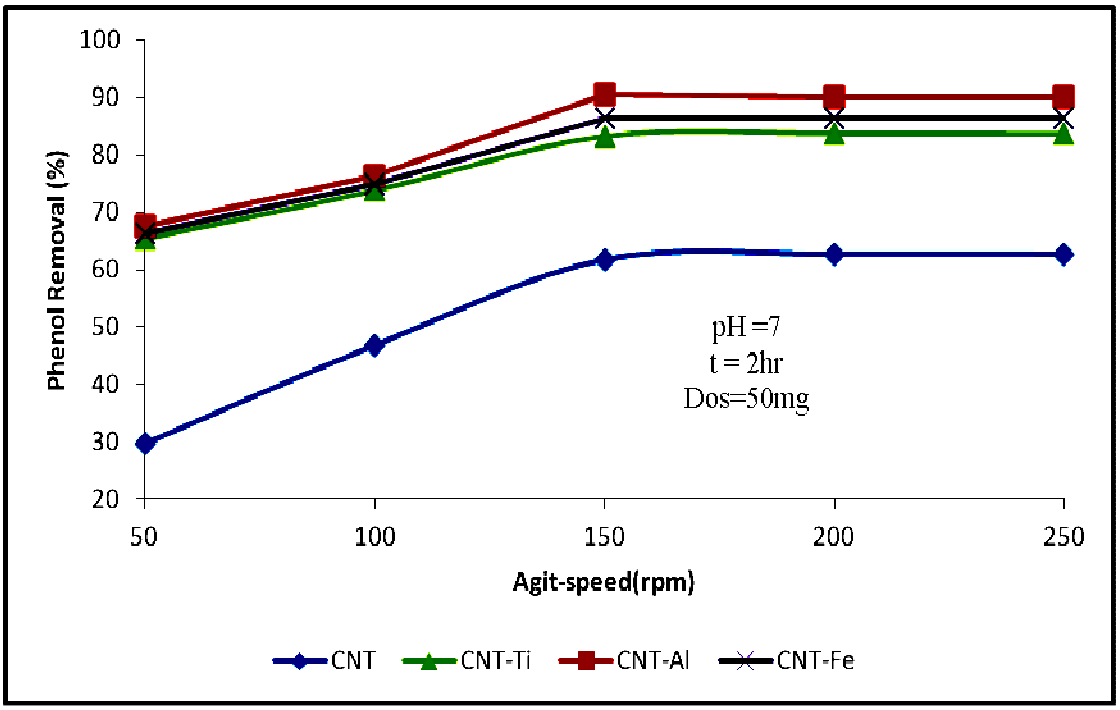


Figure 4-22 : Effect of agitation speed on phenol removal efficiency by raw and MCNTs

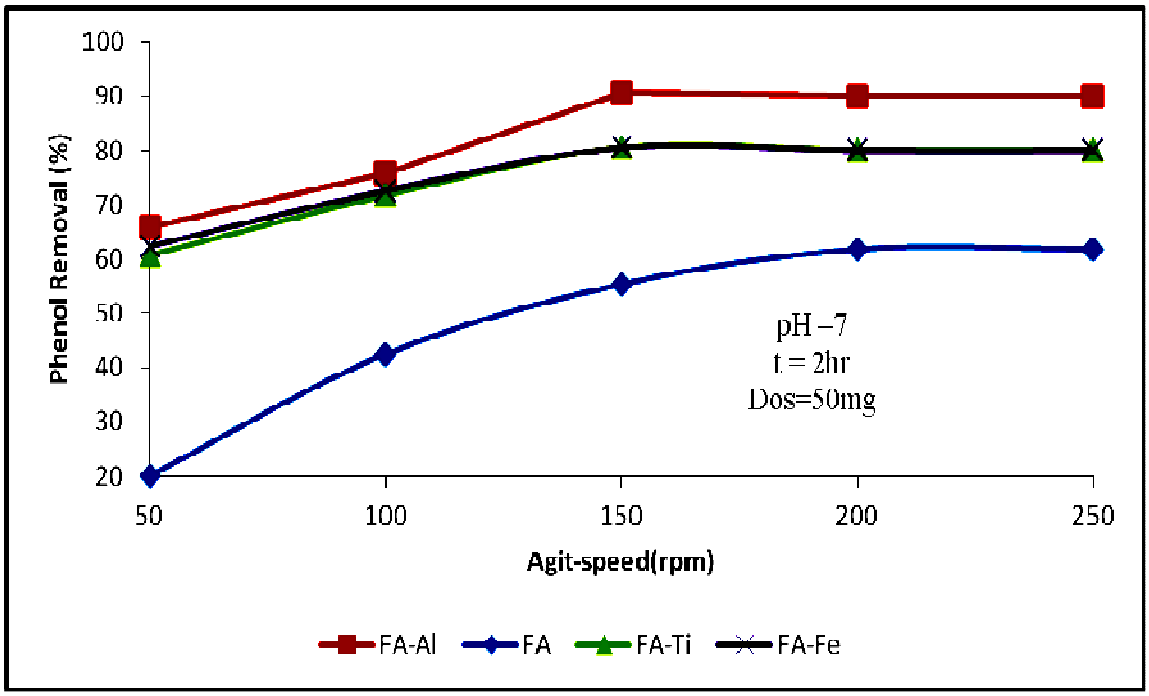


Figure 4-23 : Effect of agitation speed on phenol removal efficiency by raw and MFA

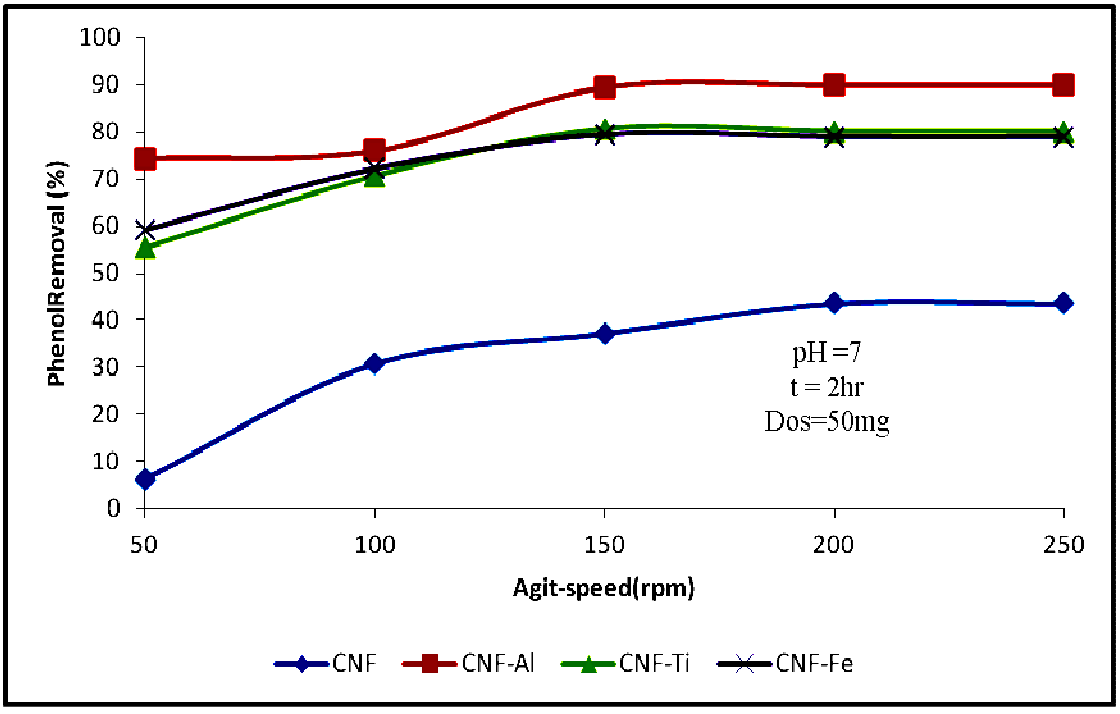


Figure 4-24 : Effect of agitation speed on phenol removal efficiency by raw and MCNFs

4.2.1.4 Effect of Adsorbent Dosage Rate

Due to the fact that the amount of the adsorbent in the solution has a great effect on the adsorption processes, a study of its effect on the adsorption capacity was carried out by using raw and modified adsorbents by taking peak removal at pH7, 2 hours contact time and 200 rpm agitation speed. The amount of the adsorbent dosage varied from 10 mg to 600 mg. It has been noticed that the increase on the dosage lead to the increase in the removal efficiency. This phenomena is due to the increasing on the sites on the surface of the adsorbents which offer high availability of exchange sites for phenol molecules. The results in Figure 4.25 indicate that the 100 % removal of phenol can be achieved by 300, 450, 600 and 500 mg for AC, CNTs, CNFs and FA, respectively.

Similar behavior was notice when using modified adsorbents at fixed pH of 7, 2 hours contact time and 200 rpm agitation speed as shown in Figures 4-26 to 4-29. The results in these figures show clearly the effect of the modification on the removal efficiency, the 100% removal of phenol was achieved by using 200 mg of AC-Al compare with 300 mg of raw AC, 250 mg of CNTs-Al compare with 400 mg of raw CNTs, 200 mg of CNFs-Al compare with 600 mg of raw CNFs and 150 of FA-Al compare with 500 mg of raw FA.

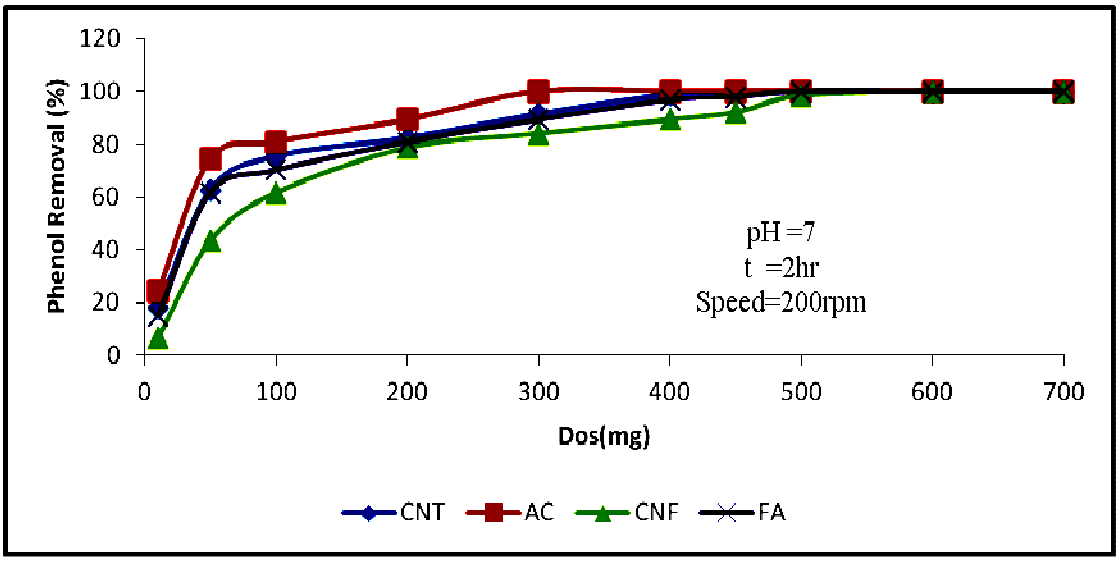


Figure 4-25 : Effect of Adsorbent dosage on phenol removal efficiency by raw CBAs

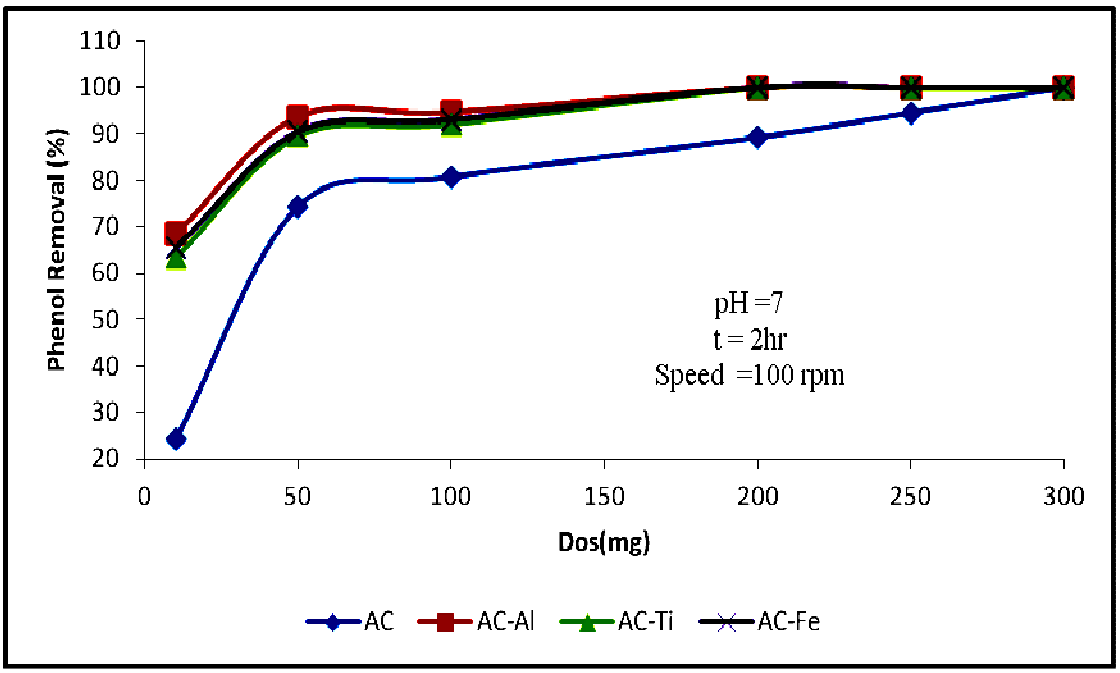


Figure 4-26 : Effect of Adsorbent dosage on phenol removal efficiency by raw and MAC

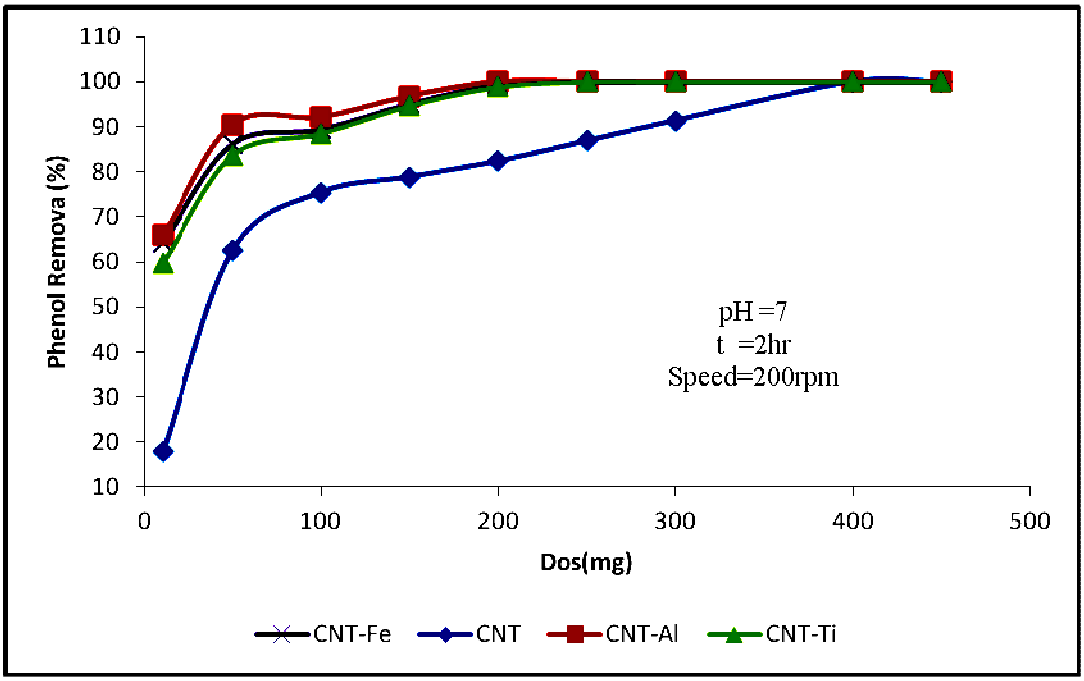


Figure 4-27 : Effect of Adsorbent dosage on phenol removal efficiency by raw and MCNTs

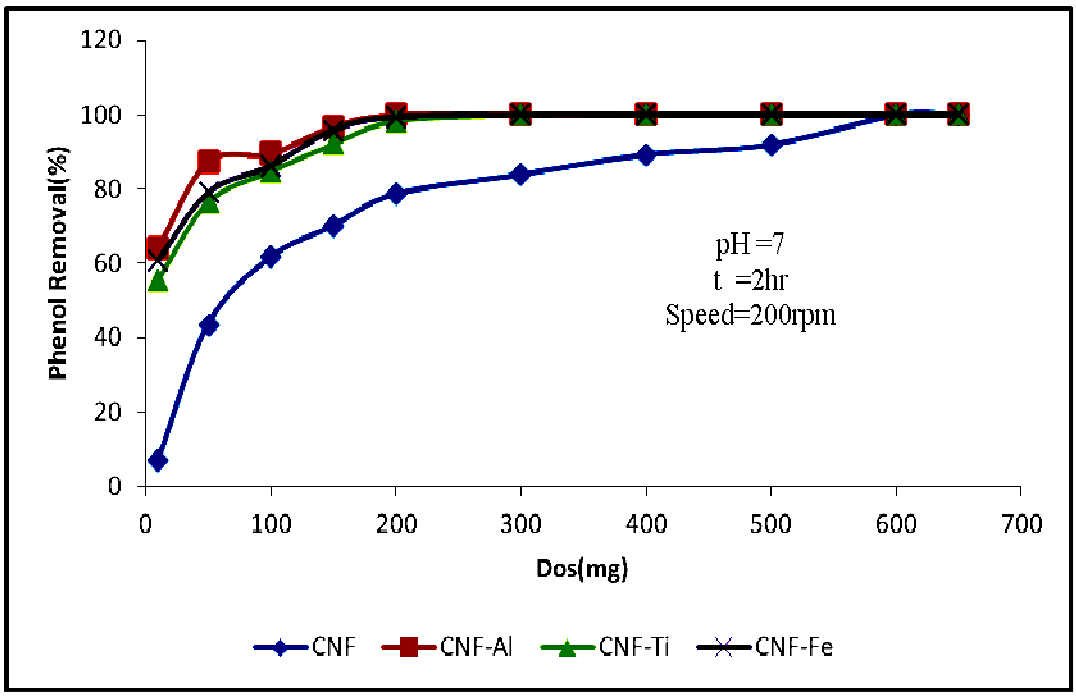


Figure 4-28 : Effect of Adsorbent dosage on phenol removal efficiency by raw and MCNFs

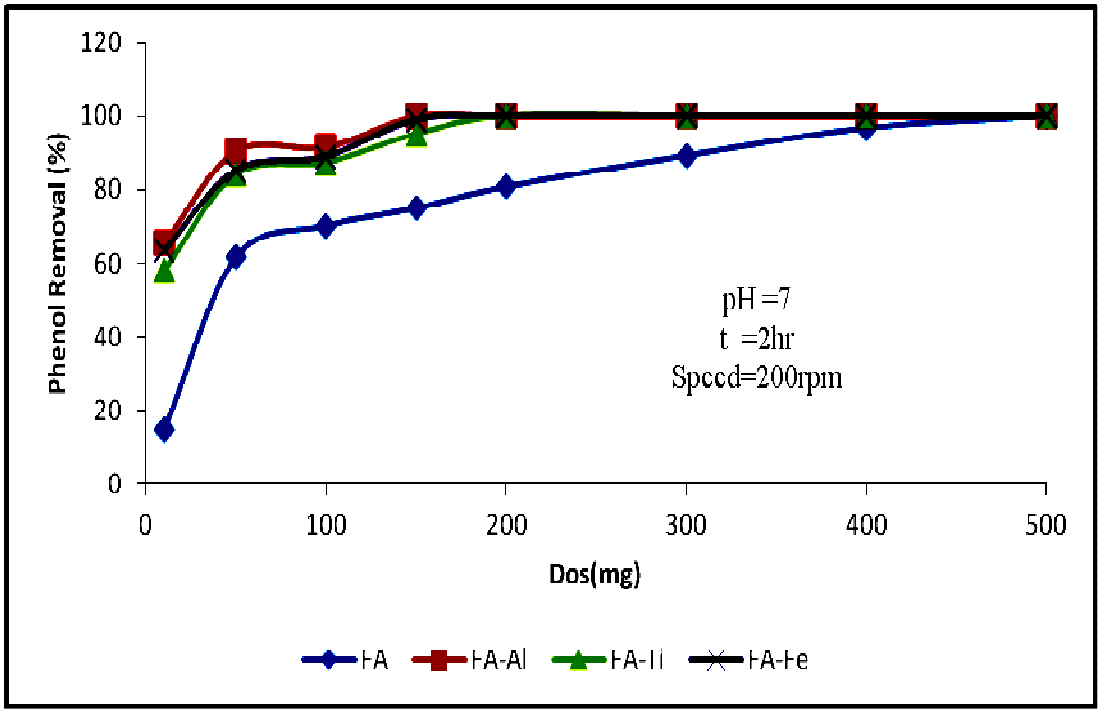


Figure 4-29 : Effect of Adsorbent dosage on phenol removal efficiency by raw and MFA

4.2.2 Removal of 4-Chlorophenol Using Carbon Based Adsorbents

The removal of 4-Chlorophenol depends on the following parameters:

4.2.2.1 Effect of pH

The removal of 4-Chlorophenol by raw and modified carbon based adsorbent with various pHs have been studied. The pH range was between 3 to 8 and the following parameters were kept constant namely, contact time of 2 hr, dosage of adsorbent of 50 mg and shacking speed of 100 rpm. The results obtained by varying the pH from 4-Chlorophenol in water solutions containing AC, CNTs, CNFs and FA adsorbents are shown in Figure 4-30. Similar phenomena of the effect of the pH were observed. In Figure 4-30, it was noticed that when pH was increased from 3 to 6, the removal of 4-Chlorophenol in the solution by all adsorbents was increased continuously and then decreased within the pH range of 6-8. At pH 6 the maximum percentage removals of 4-Chlorophenol by AC, CNTs, CNFs and FA were found to be approximately 61%, 52%, 37% and 32%, respectively. The adsorption capacity of the activated carbon is the higher than the one on the CNTs, while the adsorption capacity of CNFs and FA are very near to each other.

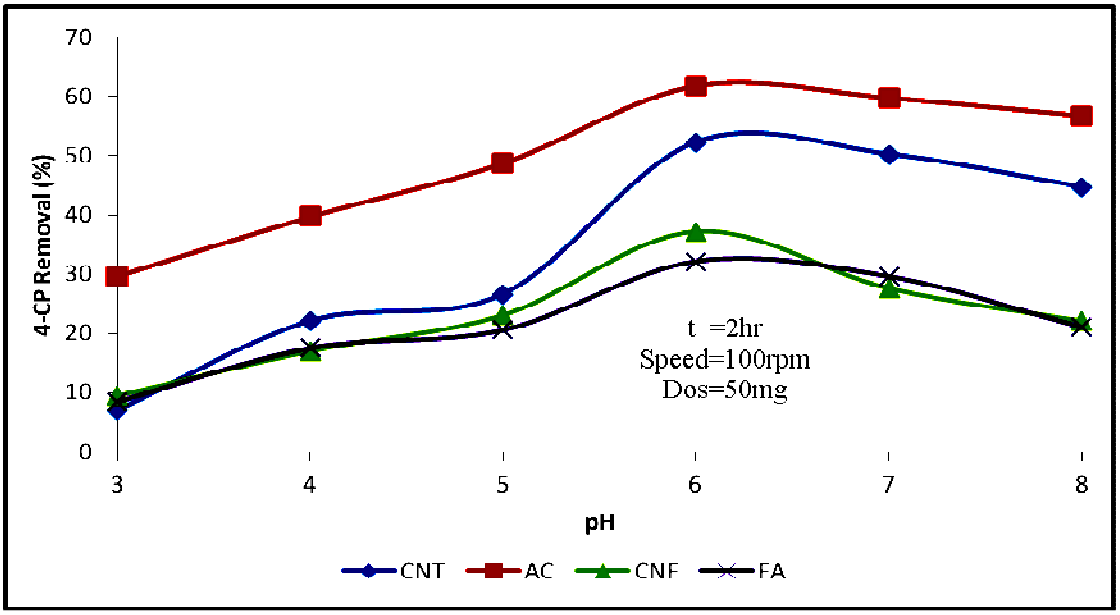


Figure 4-30 : Effect of pH on the 4-CP removal efficiency by raw CBAs

The removal of 4-Chlorophenol by MCBAs also has been studied, as shown in Figures 4-31 to 4-35. The pH was between 3to8. Similar phenomena of the effect of pH were observed for all modified adsorbent. It was notice that, with the increase of pH from 3 to 6, the removal of 4-Chlorophenol by all modified adsorbents increases. As clear from Figure 4-3, at pH 6, the maximum percentage removals of 4-Chlorophenol by AC-Al, AC-Ti and AC-Fe were found to be 77.1%, 74.6 % and 60.9%, respectively. In contrast, at pH 6, the removal by CNT-Al, CNT-Ti and CNT-Fe as shown in Figure 4-32 was found to be 76.1%, 70% and 63.4%, respectively. The same phenomena were recognized for the removal at pH 6 by modified FA and CNFs, as shown in Figure 4-33 and 4-34. The data for raw adsorbent from Figure 4-30 was introduced in the Figures 4-31 to 4-34 to show the great effect of the impregnated metals on the removal efficiency.

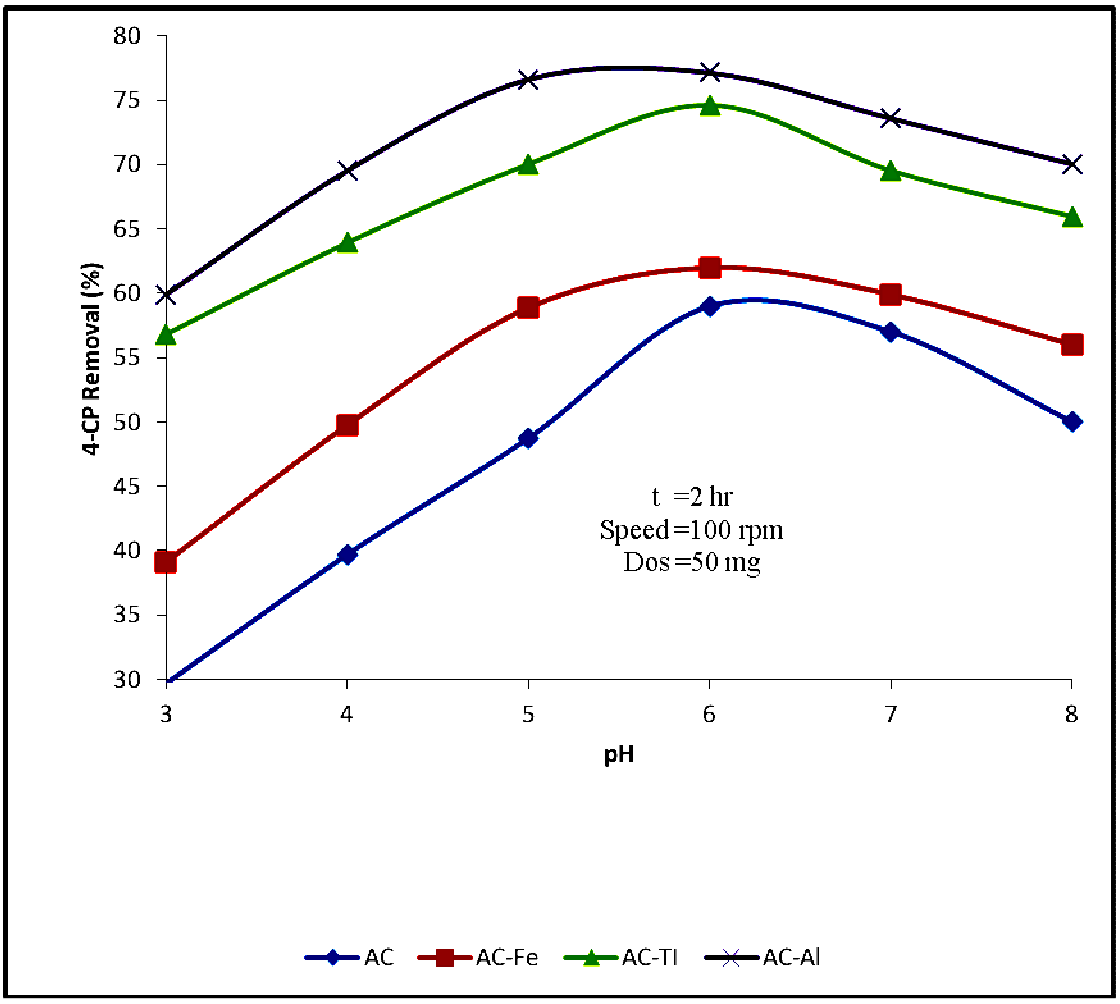


Figure 4-31 : Effect of pH on the 4-CP removal efficiency by raw and MAC

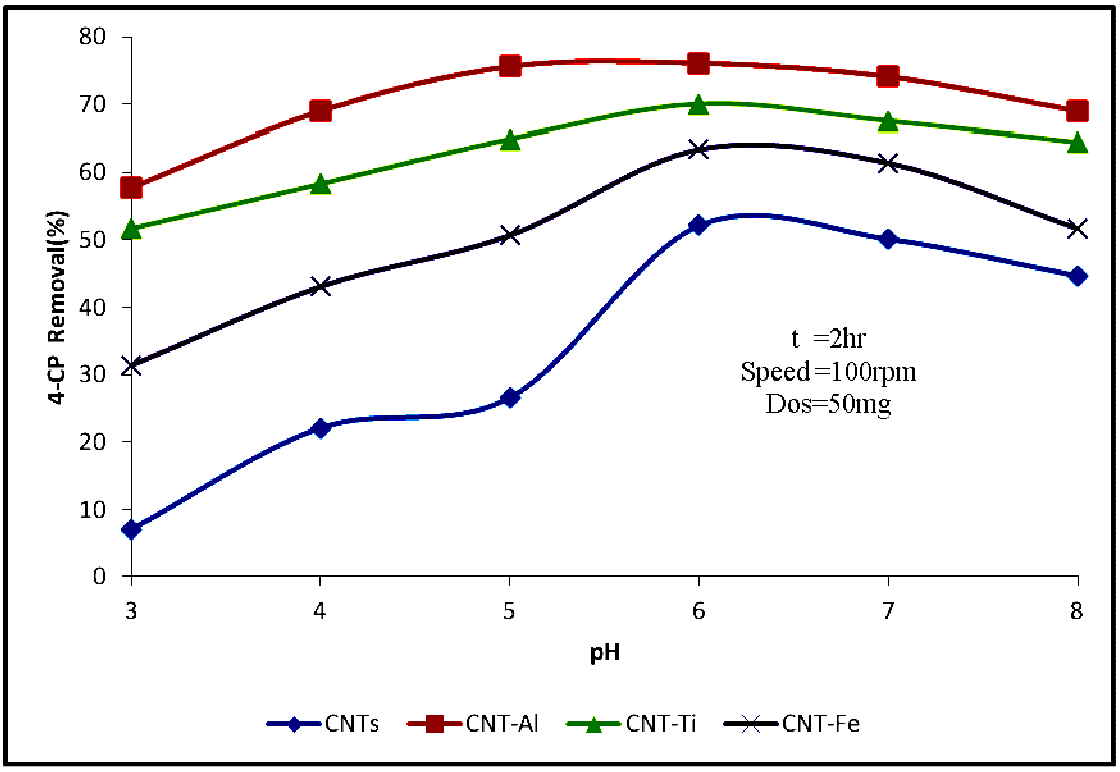


Figure 4-32 : Effect of pH on the 4-CP removal efficiency by raw and MCNTs

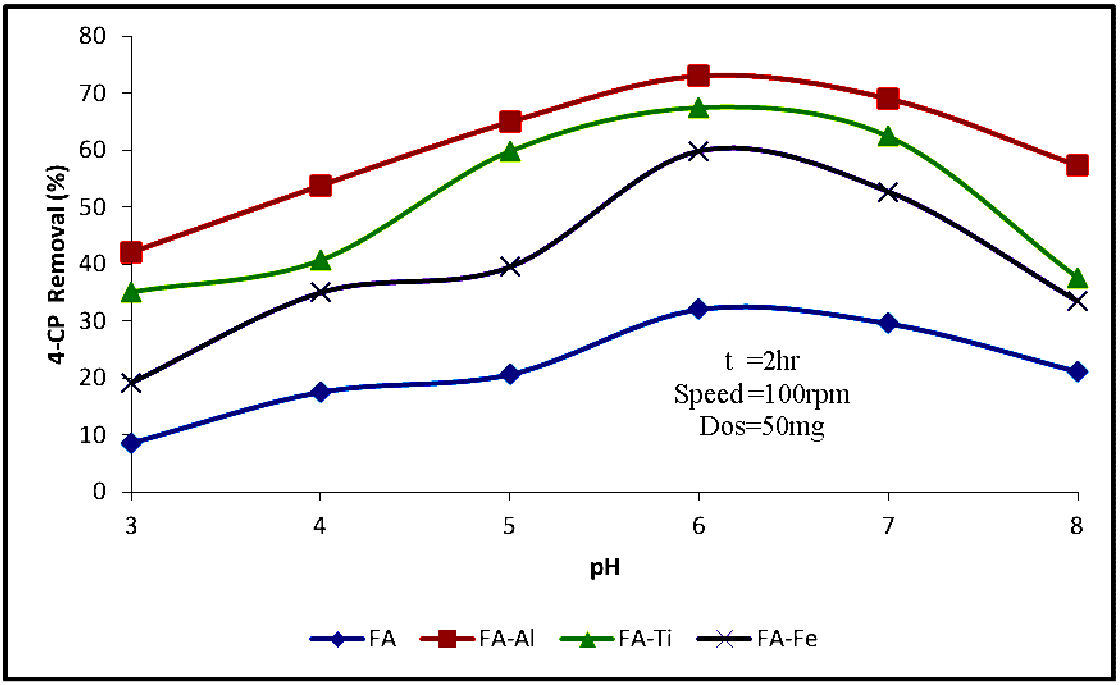


Figure 4-33 : Effect of pH on the 4-CP removal efficiency by raw and MFA

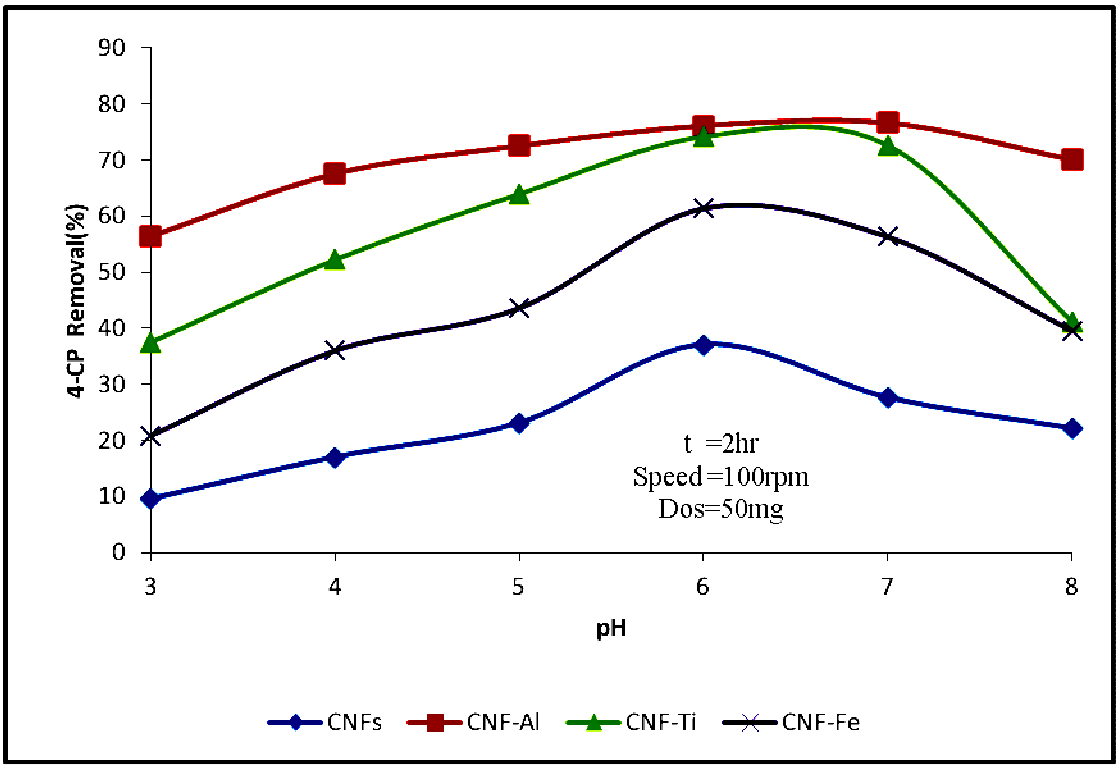


Figure 4-34 : Effect of pH on the 4-CP removal efficiency by raw and MCNFs

4.2.2.2 Effect of Contact time

The adsorption behavior of the 4-Chlorophenol by raw and modified carbon based adsorbents has been also studied. The experimental work were carried out by varying the experiment time from 10 minutes to 12 hours and keep the other parameter constant at pH 6,100 rpm agitation speed and 50 mg adsorbent dosage. The amount of 4-Chlorophenol adsorbed on to the raw carbon based adsorbents is shown in Figure 4-35. The removal increased rapidly during the first 2 hours, after which the removal remains constant for up to 12 hours. The same phenomenon was observed by using Modified AC, CNTs, FA and CNFs as shown in Figures 4-36 to 4-39, respectively.

From the adsorption behavior of the 4-chlorophenol on the modified and raw adsorbents, it was concluded that two hours is the optimum time for the best removal. After that, the removal remains constant which indicates that the 4-Chlorophenol is

difficult to desorbed back to the bulk solution. The effect of the modified adsorbents was also noticed which lead to increase the removal efficiently of the 4-Chlorophenol.

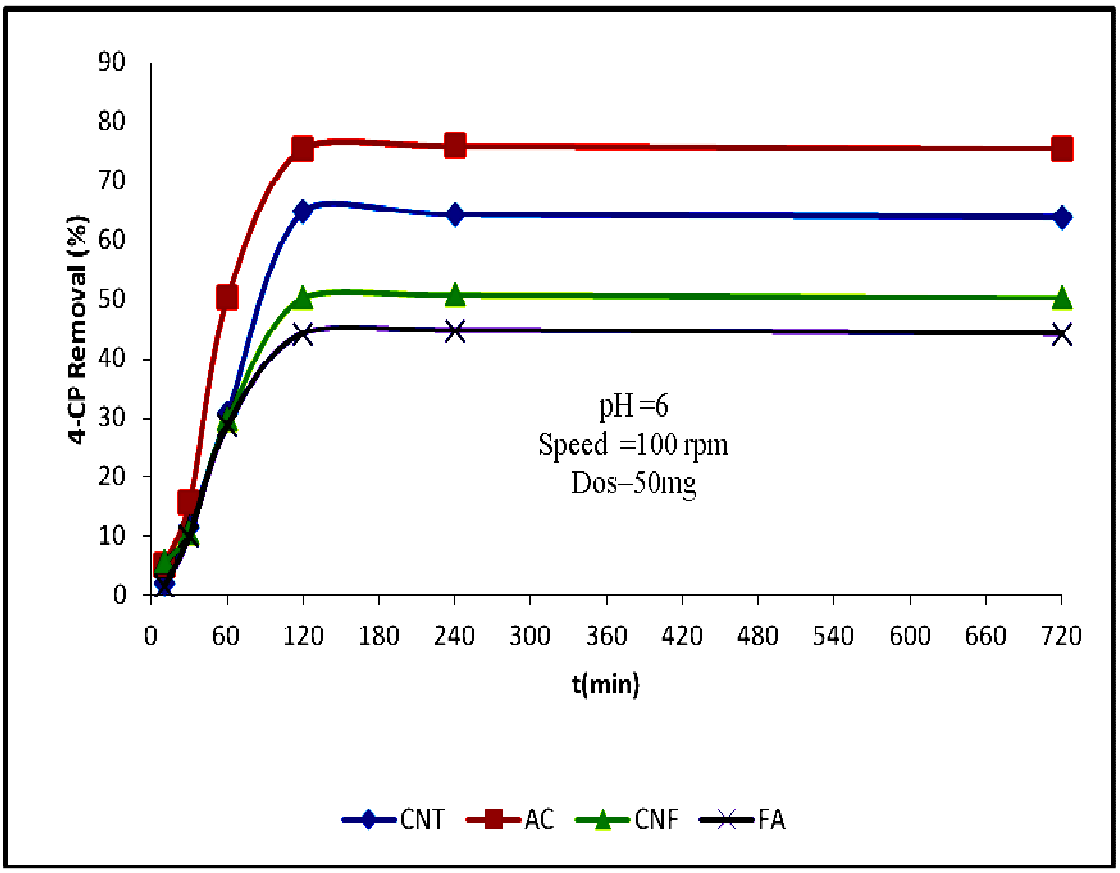


Figure 4-35 : Effect of contact time on the 4-CP removal efficiency by raw CBAs

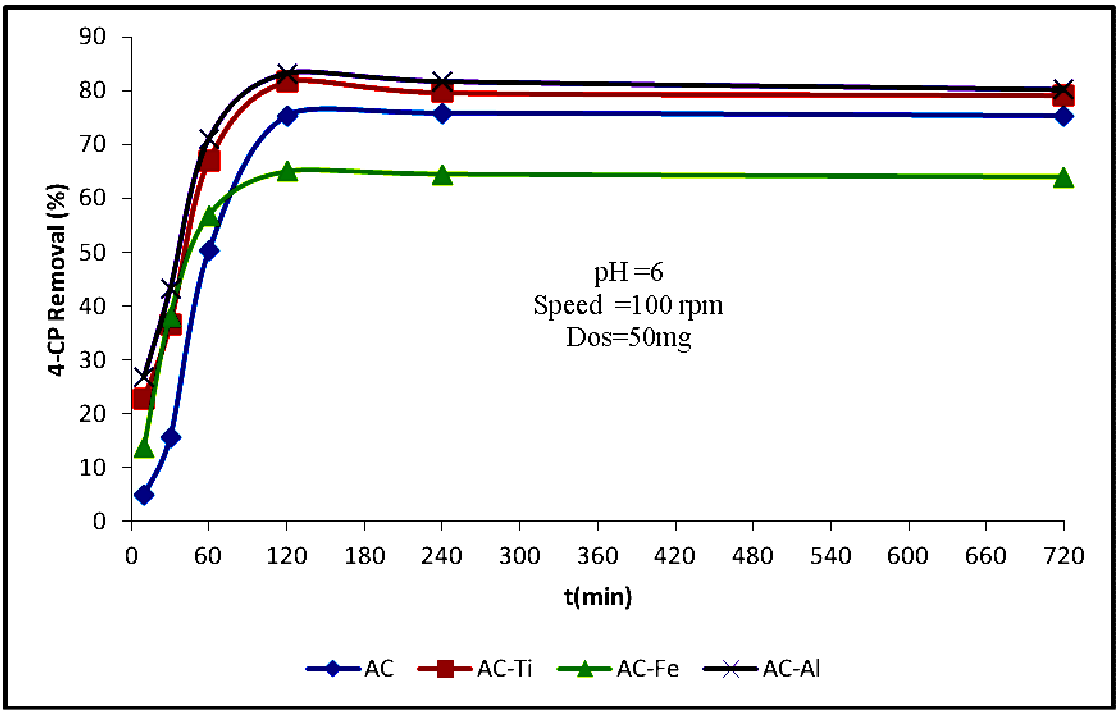


Figure 4-36 : Effect of contact time on the 4-CP removal efficiency by raw and MAC

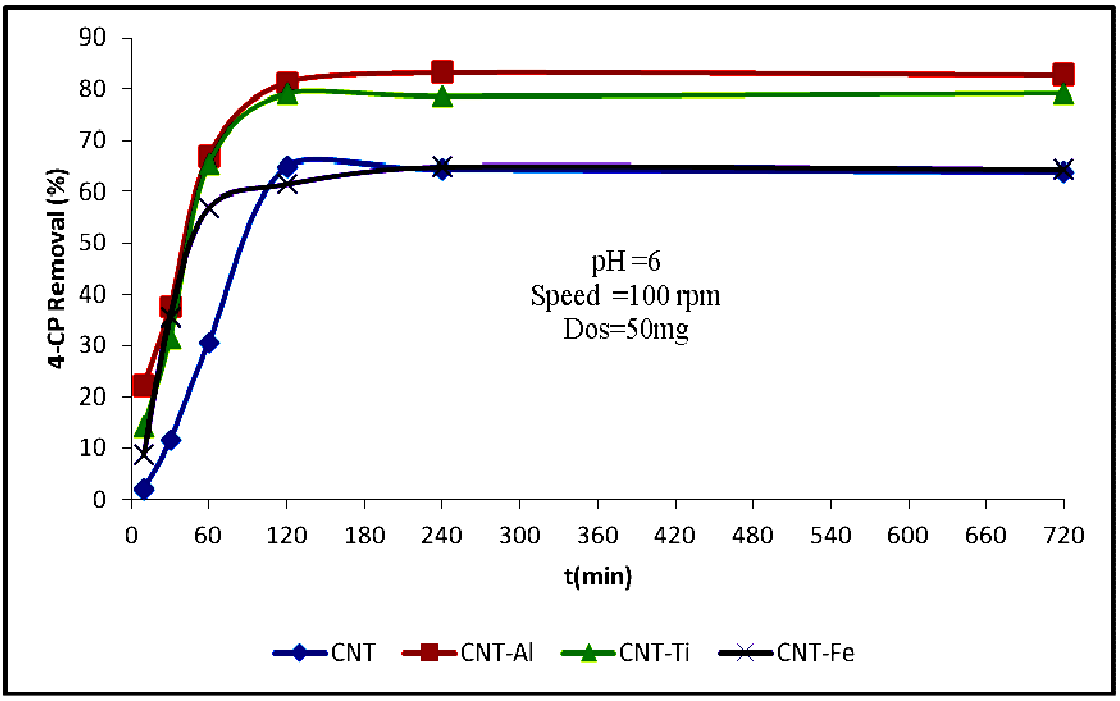


Figure 4-37 : Effect of contact time on the 4-CP removal efficiency by raw and MCNTs

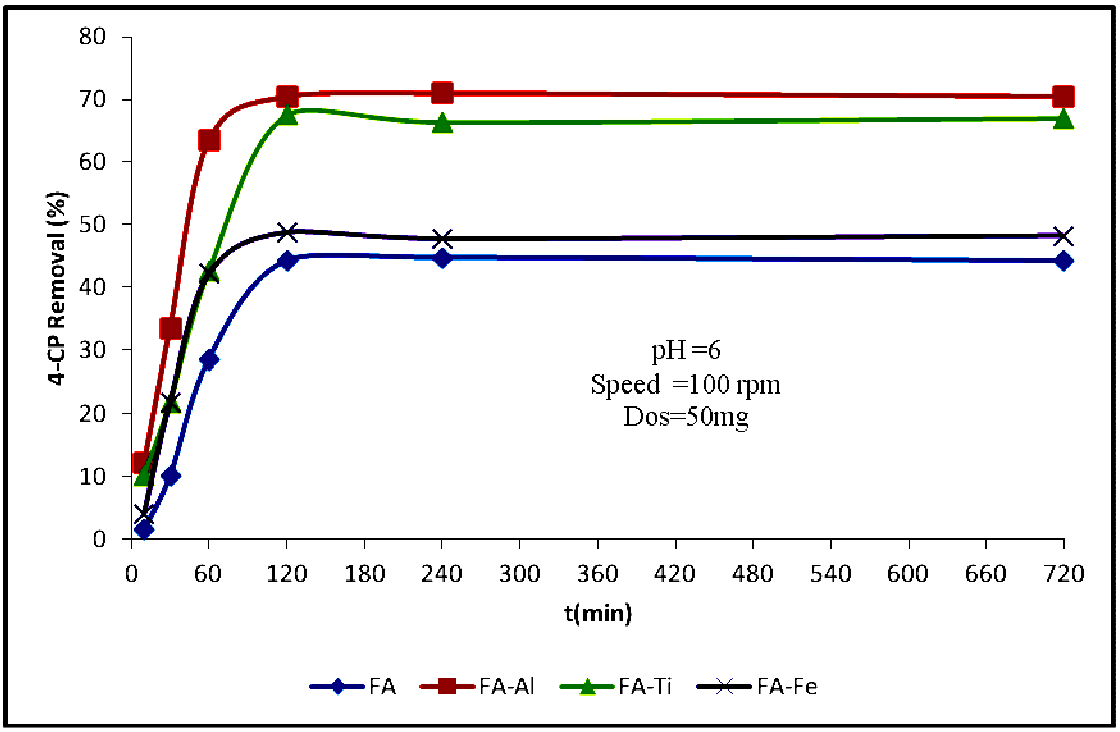


Figure 4-38 : Effect of contact time on the 4-CP removal efficiency by raw and MFA

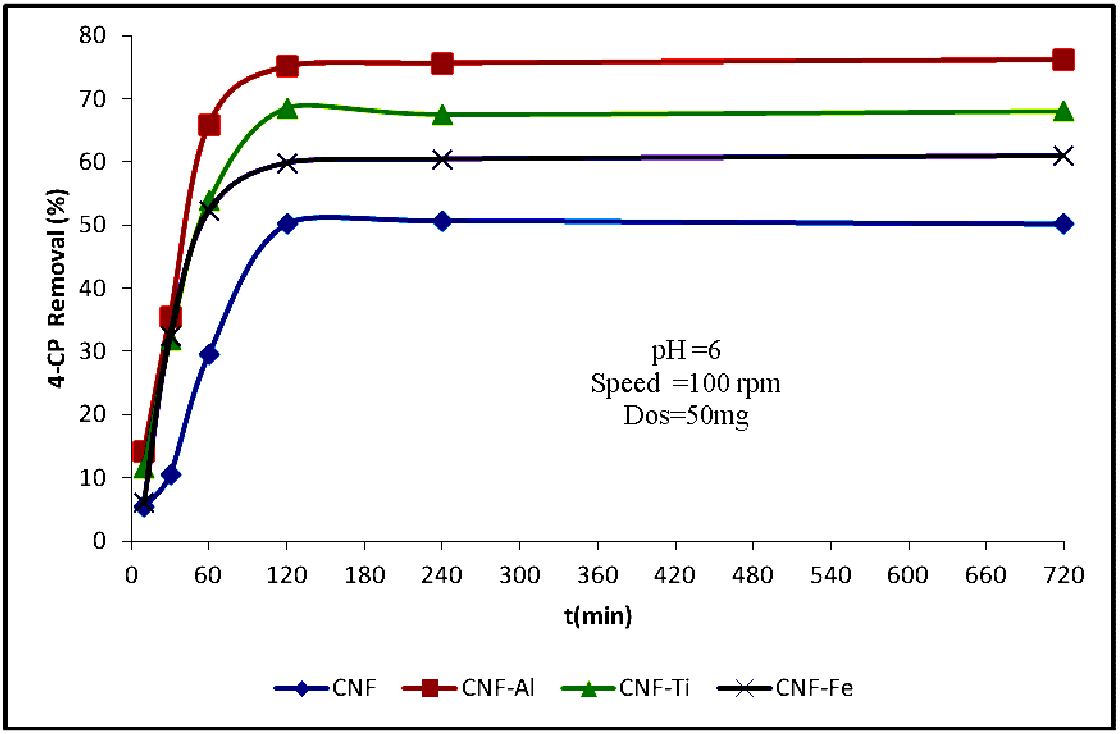


Figure 4-39 : Effect of contact time on the 4-CP removal efficiency by raw and MCNF

4.2.2.3 Effect of Agitation speed

The peak removal at pH 6 and two hours of contact time was used to study the effect of the agitation speed on the adsorption capacity of the 4-Chlorophenol by raw CBAs. By varying the agitation speed from 50 to 250 rpm as shown in Figure 4-40, it has been observed that the percentage of removal was increased slightly by increasing the agitation speed until it reaches the maximum at 150 rpm by all adsorbents. The increase on the agitation speed improve the diffusion of 4-Chlorophenol on the adsorbents surfaces and reducing the mass transfer resistance, thus offer external mass transfer rate of 4-CP, which lead to increase in the adsorption capacity. From Figure 4-40, it can be concluded that the contact between solid and liquid was best at 150 rpm for 4-Chlorophenol removal under the removal condition stated in this work.

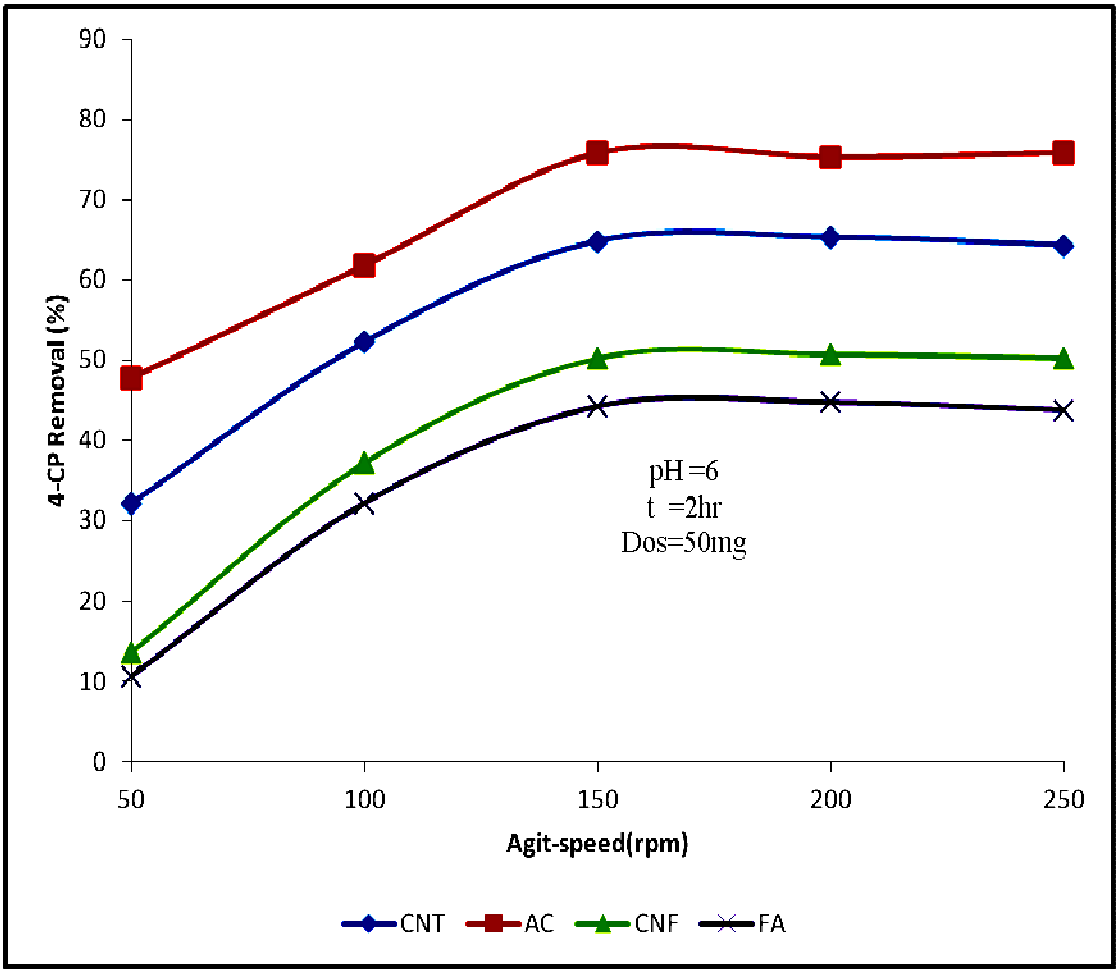


Figure 4-40 : Effect of agitation speed on the 4-CP removal efficiency by raw CBAs

Similarly, the peak removal at 2 hours contact time and pH 6 was used to study the effect of the agitation speed on the adsorption capacity of the 4-Chlorophenol by modified adsorbents as shown in Figures 4-41 to 4-44. It has been observed that the removal percentage was increased with increasing speed up to 150 rpm for all modified adsorbents. Then, the removal remained constant with the increase in the agitation speed. The effect of the modified adsorbents on the removal of the 4-CP can be clearly seen if we compare Figure 4.40 with Figures 4-41 to 4-44. The impregnation of aluminum gave the best removal. From the Figure 4-41 to 4-44, it can be concluded that the contact between solid and liquid is the best at 150 rpm for 4-chlorophenol removal under the removal condition stated in this work for all modified adsorbents. On the other hand, the increasing on the agitation speed more than 150 rpm will not enhance the removal any more.

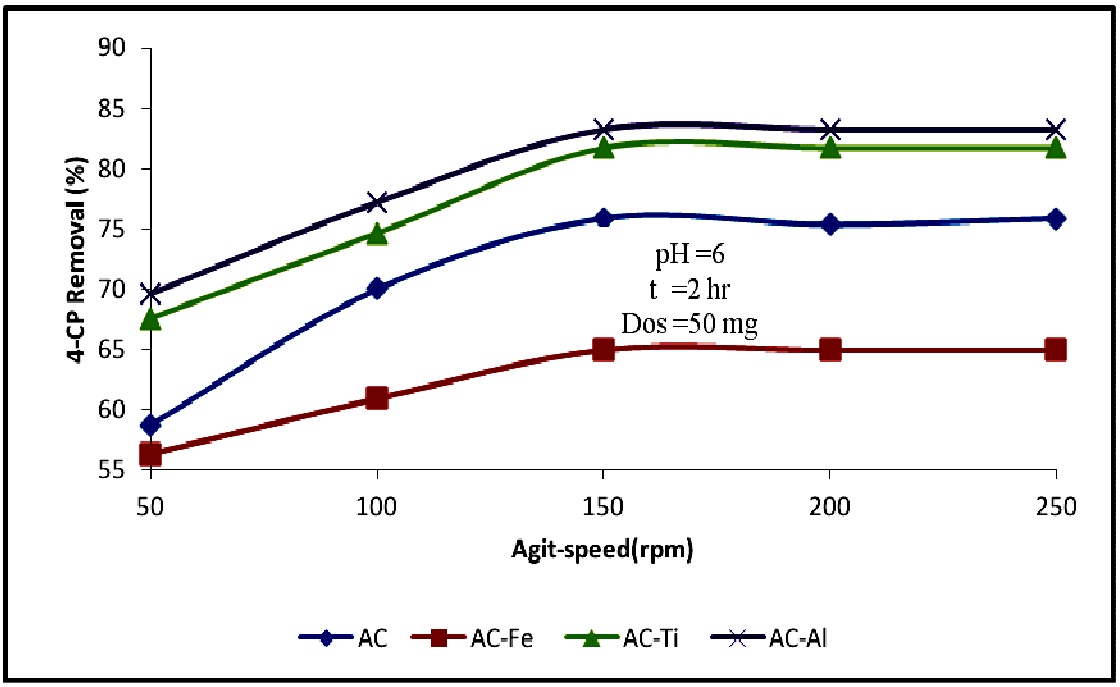


Figure 4-41 : Effect of agitation speed on the 4-CP removal efficiency by raw and MAC

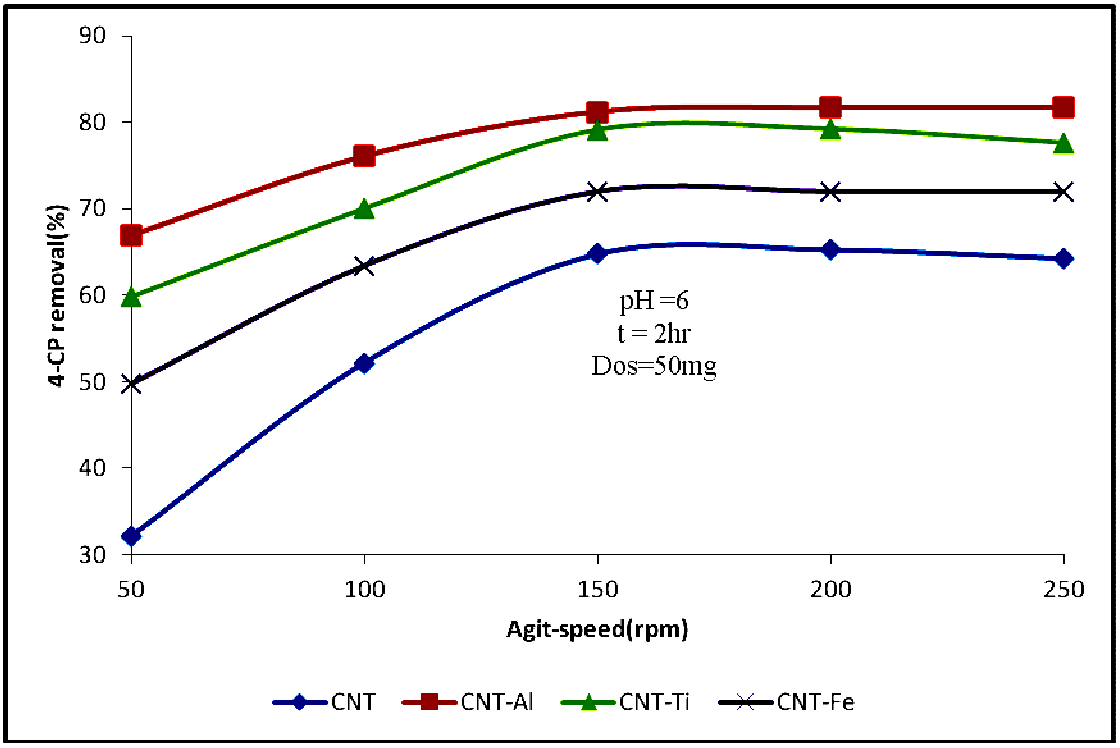


Figure 4-42 : Effect of agitation speed on the 4-CP removal efficiency by raw and MCNTs

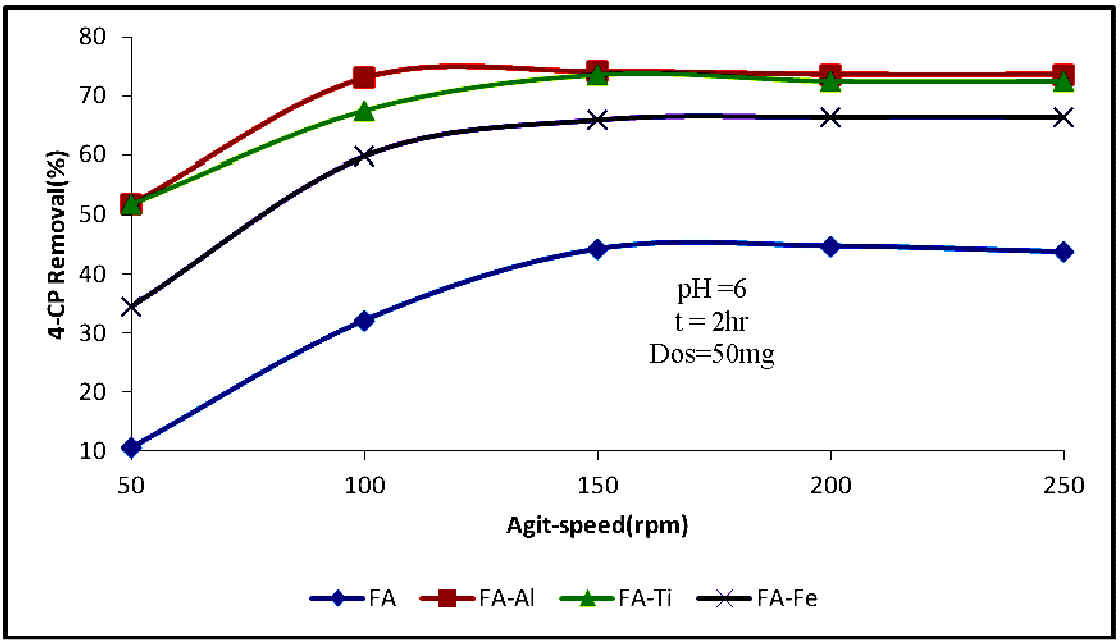


Figure 4-43 : Effect of agitation speed on the 4-CP removal efficiency by raw and MFA

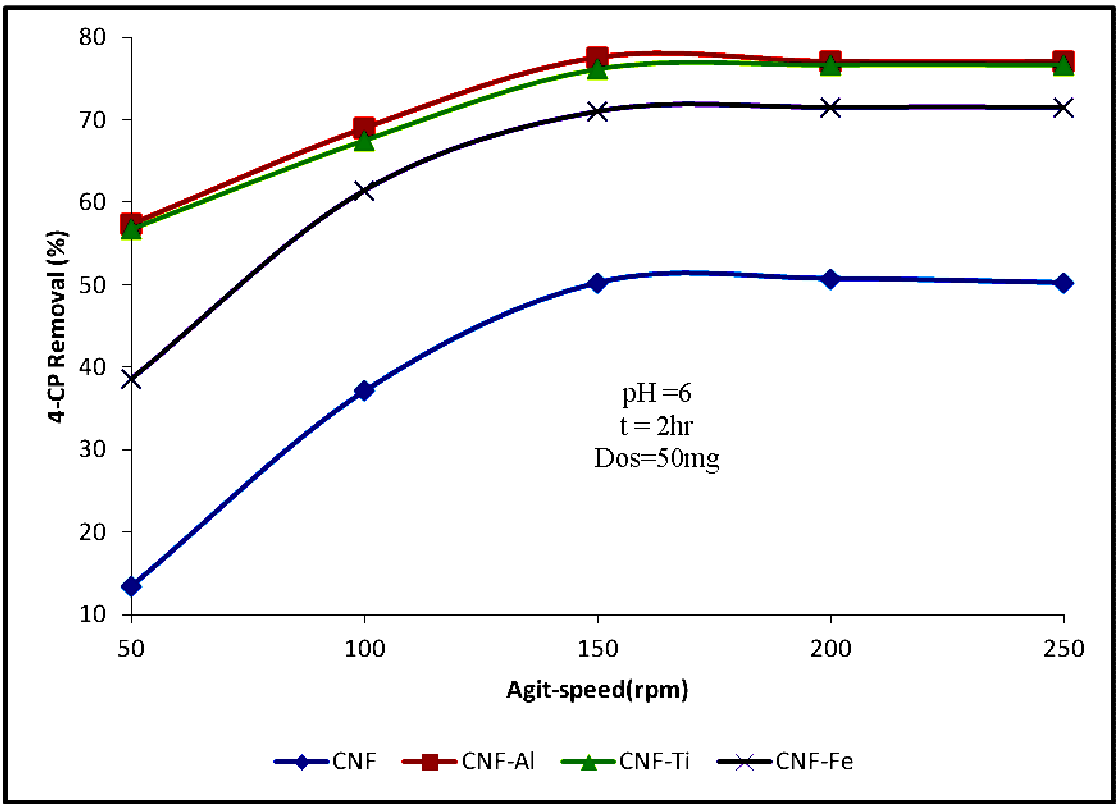


Figure 4-44 : Effect of agitation speed on the 4-CP removal efficiency by raw and MCNFs

4.2.2.4 Effect of Adsorbent Dosage Rate

By taking peak removal at pH 6, 2 hours contact time and 150 rpm agitation speed, a study of the effect of the adsorbent dosage on the adsorption of 4-Chlorophenol was carried out by using raw and modified adsorbents. The amount of the adsorbent dosage varied from 10 mg to 400 mg. It has been noticed that the increase on the dosage lead to the increase on the removal efficiency. This is due to the increasing on the vacant sites on surface of the adsorbents which offer high availability of exchange sites for 4-Chlorophenol molecules. The results in Figure 4-45 indicate that the 100 % removal of 4-Chlorophenol can be achieved by 300 mg, 400 mg, 400 mg and 500 mg of AC, CNTs, CNFs and FA, respectively.

Similar behavior was noticed when using modified adsorbents at fixed pH of 6, 2 hours contact time and 150 rpm agitation speed as shown in Figures 4-46 to 4-49. The results in these figures showed clearly the effect of the modification on the removal efficiency. The 100% removal of 4-Chlorophenol was achieved by using 200 mg, 200 mg, 200 mg and 300 mg of AC-Al, CNT-Al, CNF-Al and FA-Al compare with 300 mg, 400 mg, 400 mg and 500 mg of raw AC, CNTs, CNF and FA, respectively .

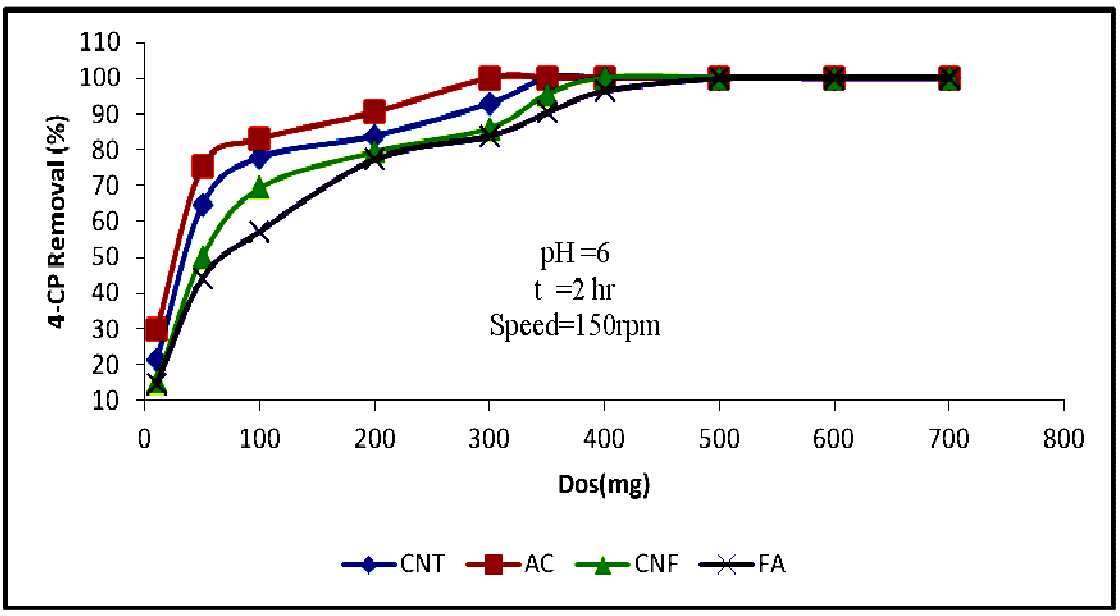


Figure 4-45 : Effect of adsorbents dosage on 4-CP removal efficiency by raw CBAs

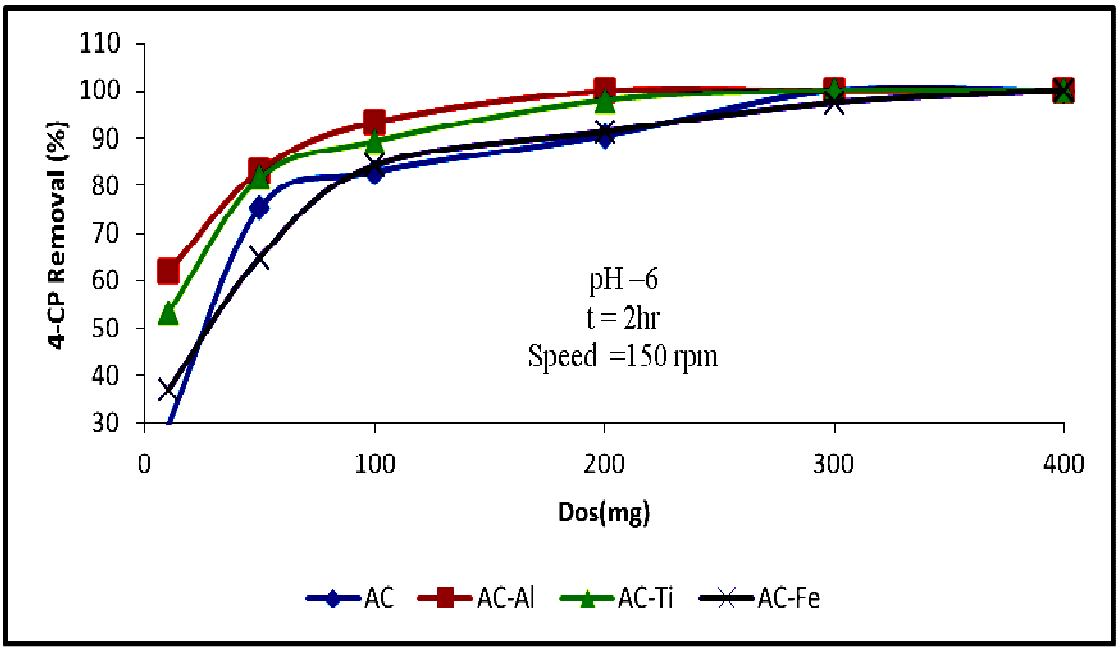


Figure 4-46 : Effect of adsorbents dosage on 4-CP removal efficiency by raw and MAC

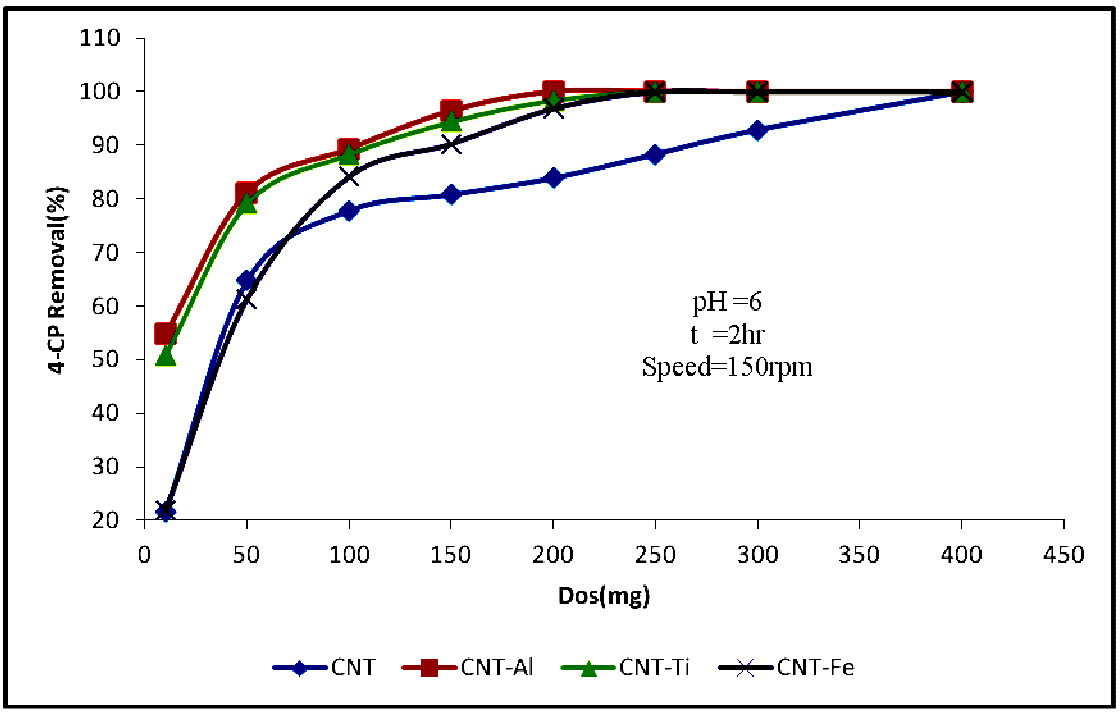


Figure 4-47 : Effect of adsorbents dosage on 4-CP removal efficiency by raw and MCNTs

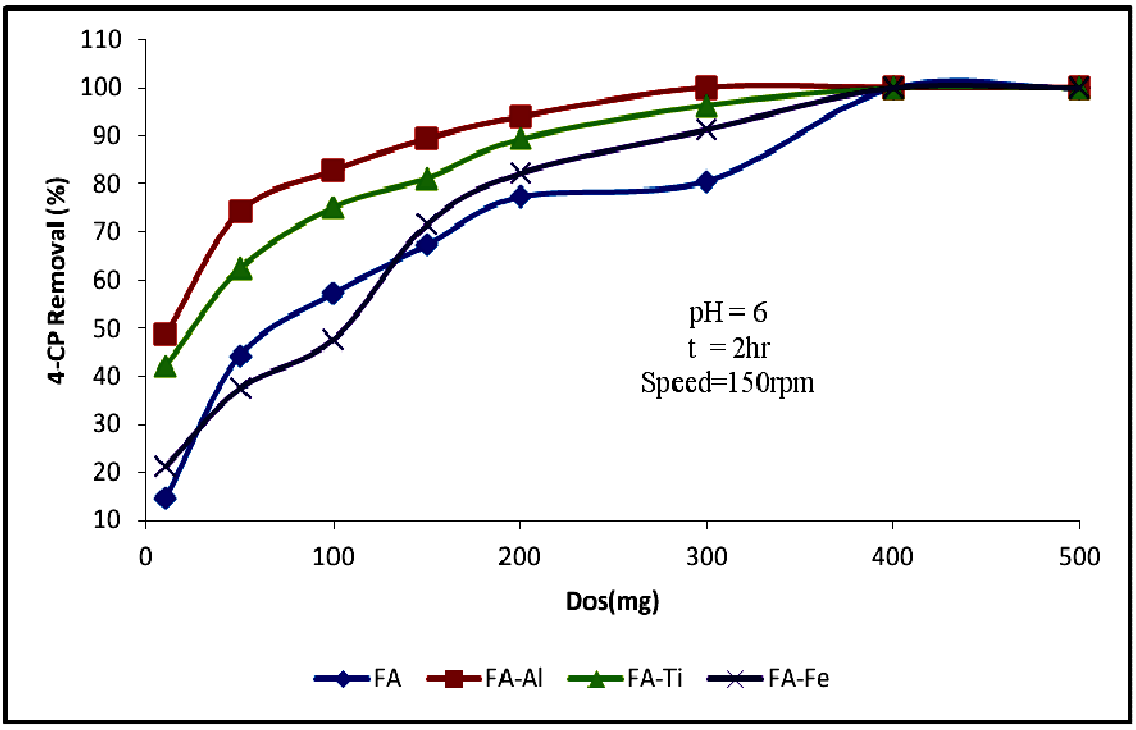


Figure 4-48 : Effect of adsorbents dosage on 4-CP removal efficiency by raw and MFA

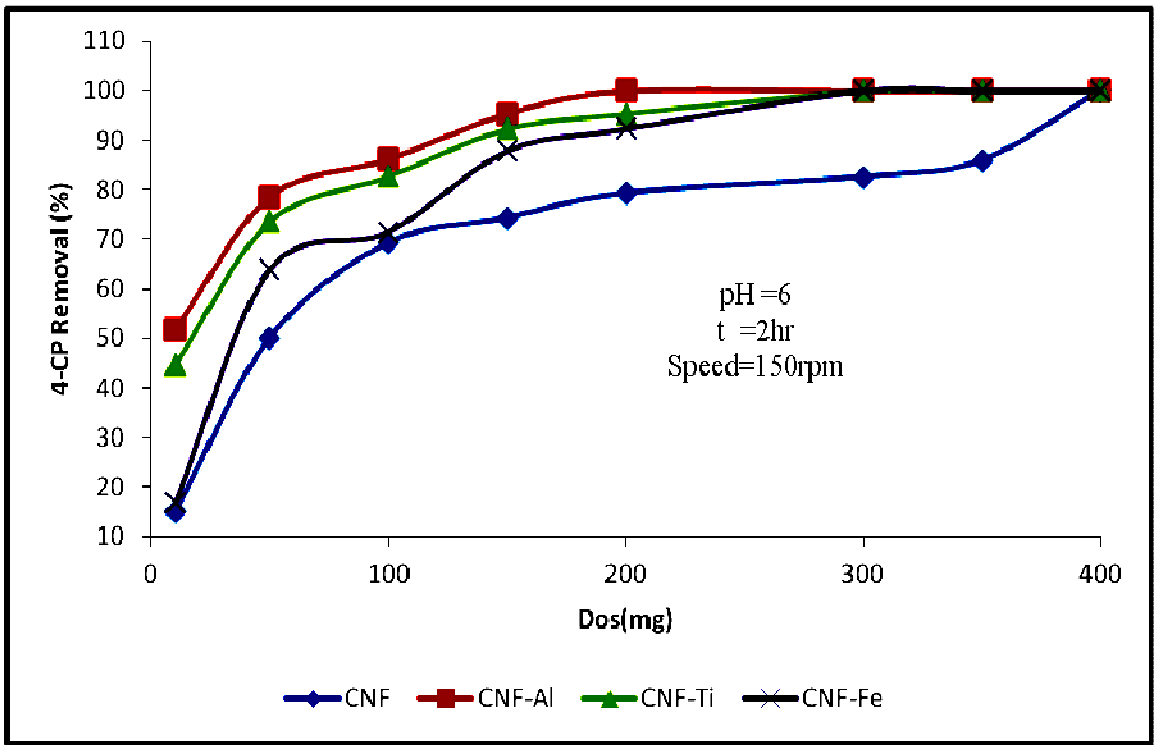


Figure 4-49 : Effect of adsorbents dosage on 4-CP removal efficiency by raw and MCNFs

4.3 Freundlich and Langmuir Isotherms Models

At set temperature, the adsorption of molecules on a solid surface to the adsorption of a medium above the solid surface related to Freundlich and Langmuir Isotherms. The experimental data of phenol and 4-Chlorophenol adsorption on the four adsorbents (raw and modified by aluminum) could be approximately by the isotherm models of Langmuir (1) and Freundlich (2).

$$\frac{C_e}{Q_e} = \frac{Q_m(K_L C_e)}{(1 + K_L C_e)} \quad \text{---------- (1)}$$

$$Q_e = K_F (C_e)^{1/n} \quad \text{---------- (2)}$$

Equation (1) and (2) in linearization form:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad \text{---------- (3)}$$

$$\text{Log} Q_e = Log K_f + \left(\frac{1}{n}\right) Log(C_e) \quad \text{---------- (4)}$$

4.3.1 Adsorption Isotherm Models for Phenol

The evaluation of the maximum adsorption capacity of the adsorbents was taken from the condition which used to optimize the adsorption process parameter. The equilibrium curves were modeled in Figures 4-50 and 4-51. The Langmuir and Freundlich in equation (3) and (4) were used to identify the data derived from the adsorption of phenol by different adsorbents over the entire parameters that have been studied. Based on the Figures 4-50 and 4-51 the maximum adsorption capacity (Q_m) and adsorption intensities were determined from the slope and the intercept of each adsorbent line, respectively.

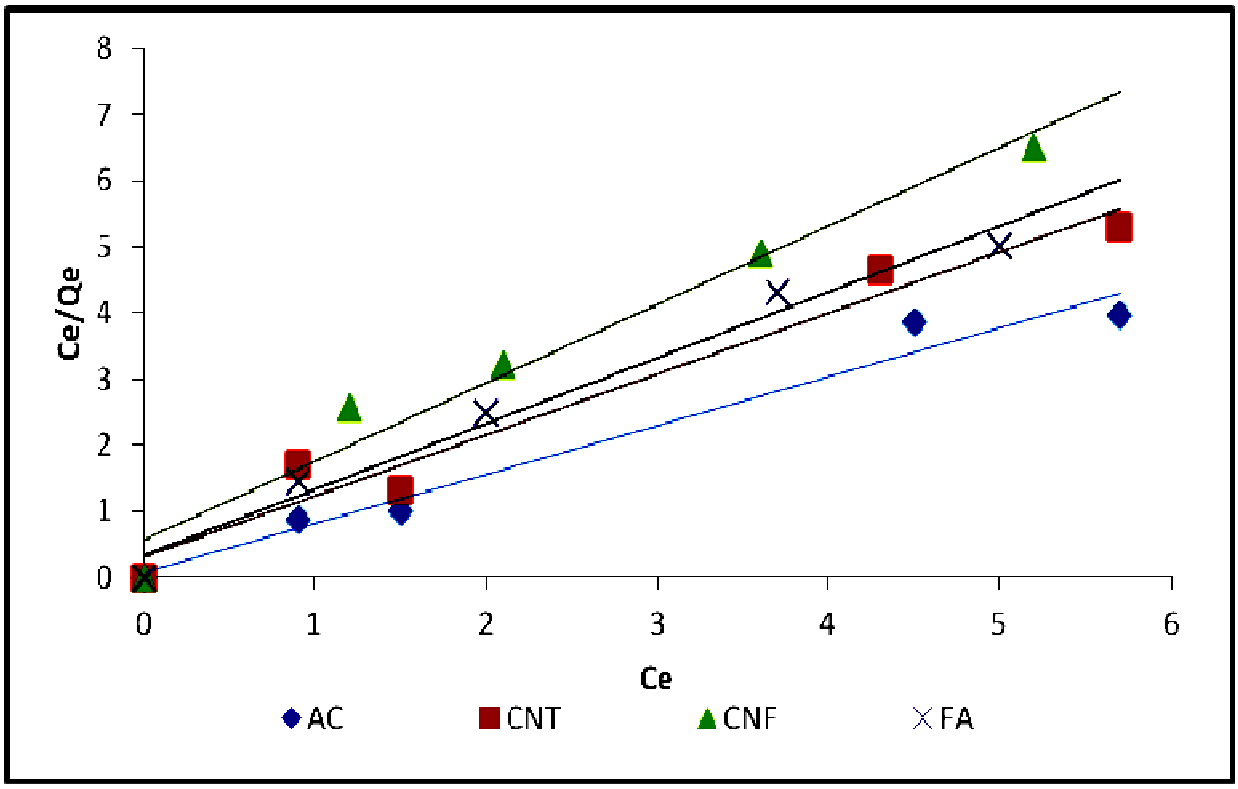


Figure 4-50 : Langmuir Adsorption isotherm model for phenol at pH 7by raw CBAs

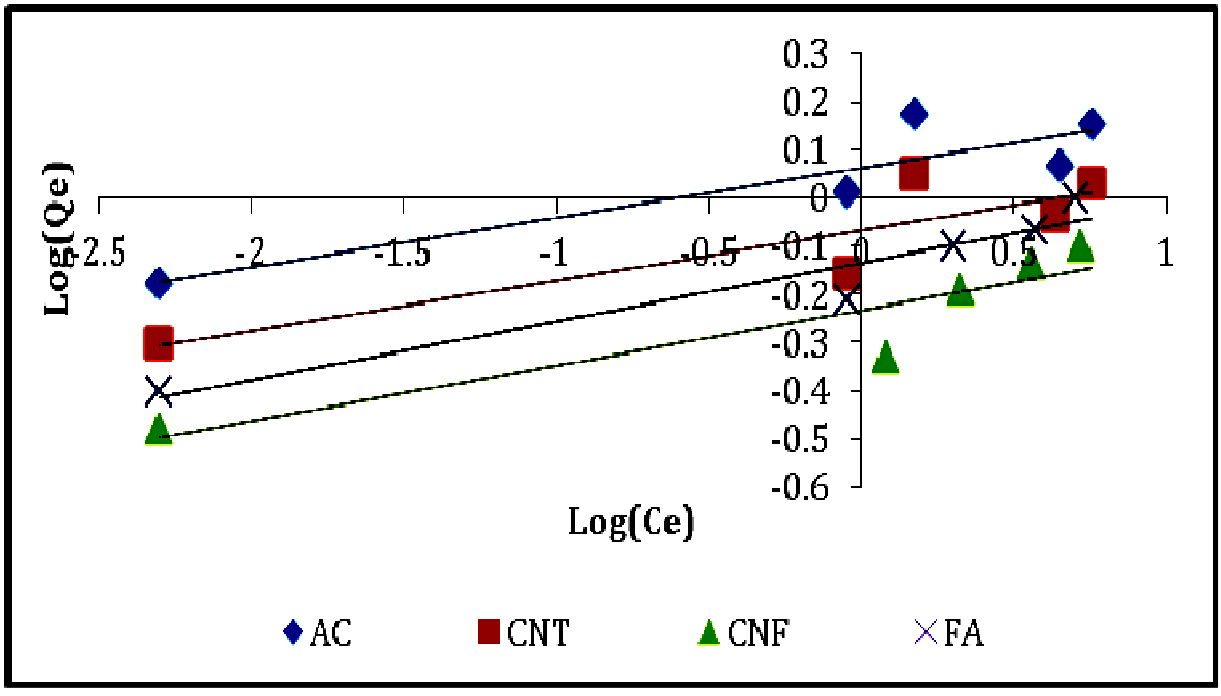


Figure 4-51 : Freundlich Adsorption isotherm model for phenol at pH7by raw CBAs

By comparing Langmuir and Freundlich isotherms from Figure 4-50 and Figure 4-51, Langmuir isotherms shows better fitting to the data with good correlation coefficients, while the Freundlich shows poor fitting to the observational data with weak correlation coefficient. Table 4-1 shows the adsorption capacity of the raw adsorbents and their correlation coefficient which are obtained from the slopes and the intercept from Figures 4-50 and 4-51. From the data on this table, it is clear that the adsorption capacity for AC is the highest, while CNFs have the lowest value of the raw adsorbents, CNTs, FA has medium adsorption capacity.

Table 4-1 : Langmuir and Freundlich Isotherm Parameters for Phenol by raw CBAs

	Langmuir			Freundlich		
Adsorbent	Q_m(mg/g)	K_L (L/mg)	R^2	n	K_F	R^2
AC	1.3477	10.911	0.973	9.803	1.1534	0.810
CNTs	1.0977	2.4037	0.961	9.615	0.861	0.787
FA	1.0070	2.8950	0.977	8.264	0.7345	0.925
CNFs	0.8418	2.1138	0.968	8.621	0.5888	0.837

The Langmuir and Freundlich equation were also used to describe the data derived from the adsorption of phenol by modified carbon based adsorbents with aluminum, due to its high removal of phenol than the other metals (Ti and Fe). Based on Figures 4-52 and 4-53 the maximum adsorption capacity (Q_m) and adsorption intensities were determined from the slope and intercept for each adsorbents line, respectively.

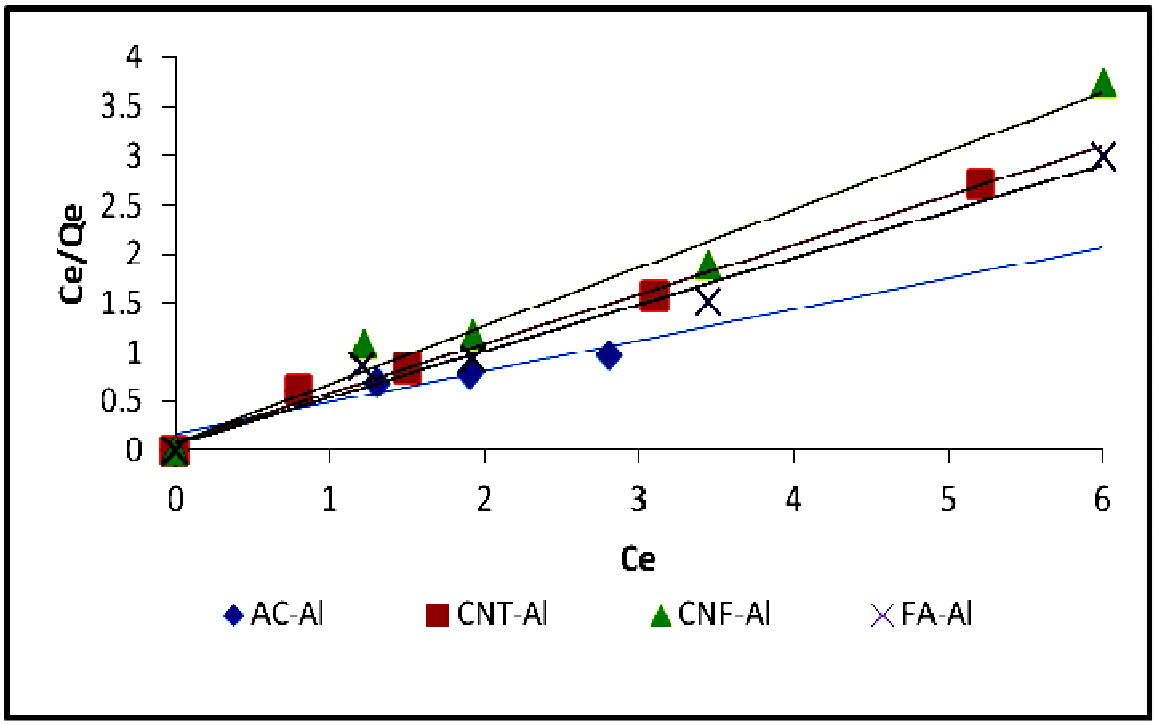


Figure 4-52 : Langmuir Adsorption isotherm model for phenol at pH7 by MCBAs

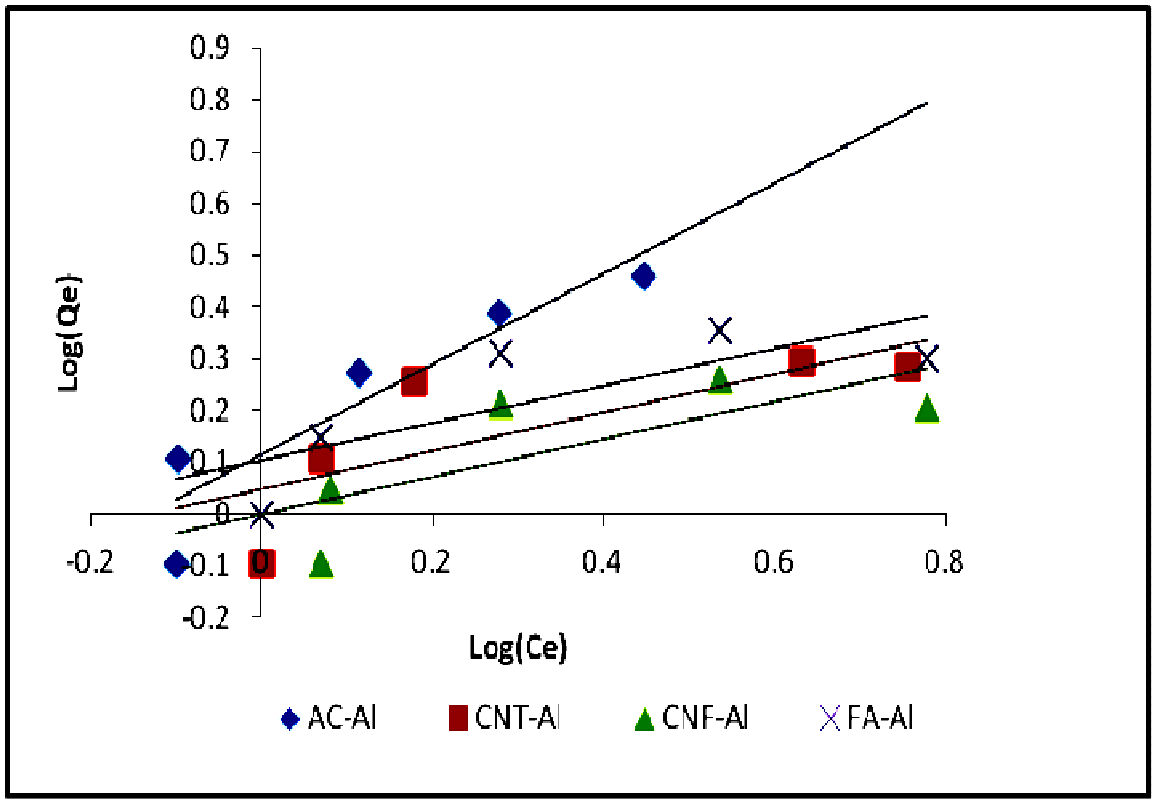


Figure 4-53 : Freundlich Adsorption isotherm model for phenol at pH7 by MCBAs

By comparing Langmuir and Freundlich isotherms from Figures 4-52 and 4-53, Langmuir isotherms shows better fitting for the CNT-Al, CNF-Al and FA-Al with high correlation coefficients. The Freundlich shows poor fitting with low values of the correlation coefficient. Table 4-2 shows the adsorption capacity of the modified adsorbents and their correlation coefficient. From the data on this table, it is clear that the adsorption capacity for AC-Al has the highest value, which indicates that the AC-Al is very efficient on the adsorption of phenol. On the other hand, the adsorption capacity value of CNF-Al is low compared with AC-Al, while the CNT-Al and FA-Al showed good values of maximum adsorption capacity. The adsorption capacity of the modified adsorbents and their correlations can show it in Table 4-2.

Table 4-2: Langmuir and Freundlich Isotherm Parameters for Phenol by MCBAs

	Langmuir			Freundlich		
Adsorbent	Q_m(mg/g)	K_L(L/mg)	R^2	n	K_F	R^2
AC-Al	3.174	1.712	0.836	1.146	1.300	0.861
CNTs -Al	2.000	5.747	0.993	2.681	1.111	0.600
FA -Al	2.105	7.196	0.979	2.786	1.265	0.625
CNFs-Al	1.684	7.156	0.979	2.747	0.995	0.568

In general, we conclude that the adsorption of phenol by raw and modified CBAs with aluminum showed a better description of Langmuir Model than the Frendlich Model.

4.3.2 Adsorption Isotherm Models for 4 – Chlorophenol

The equilibrium studies of 4-Chlorophenol adsorption indicate the maximum capacity of the adsorbents during the treatment processes by taking into account at pH 6 , the maximum removal value was achieved. Thus, this condition was used to optimize the adsorption parameter; the equilibrium curve was modeled in Figures 4-54 and 4-55. Also, the Langmuir and Freundlich in equation (3) and (4) were used to describe the data

derived from the adsorption of 4-CP by different adsorbents over the entire parameters range studied .Based on the Figures 4-54 and 4-55 the maximum adsorption capacity (Q_m) and adsorption intensities were determined from the slope and the intercept of each adsorbent line, respectively.

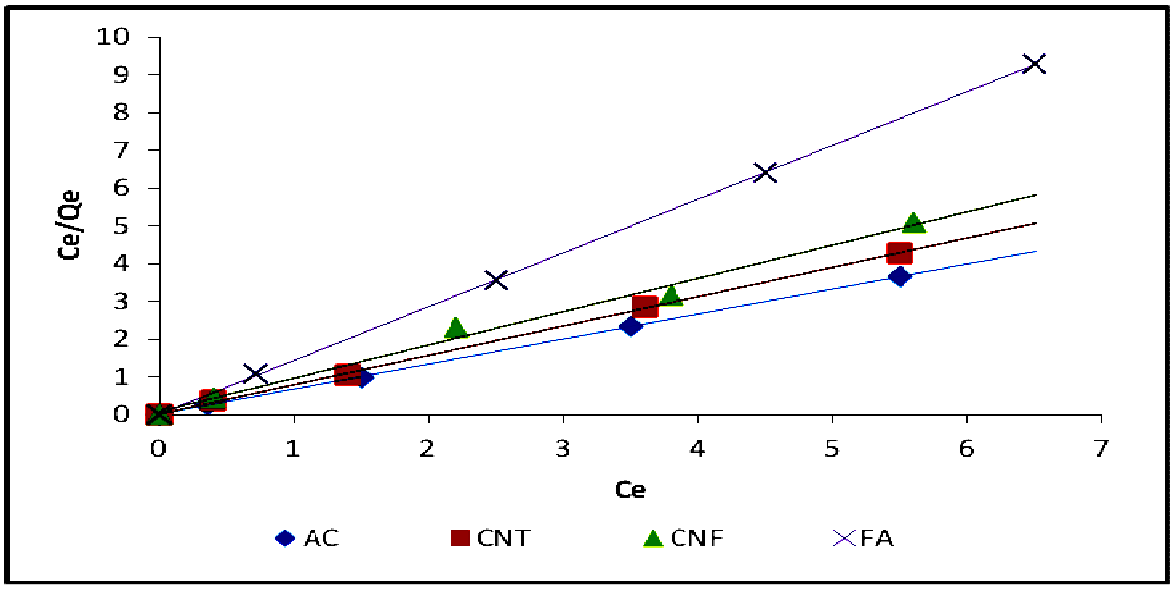


Figure 4-54 : Langmuir Adsorption isotherm model for 4-CP at pH 6 by raw CBAs

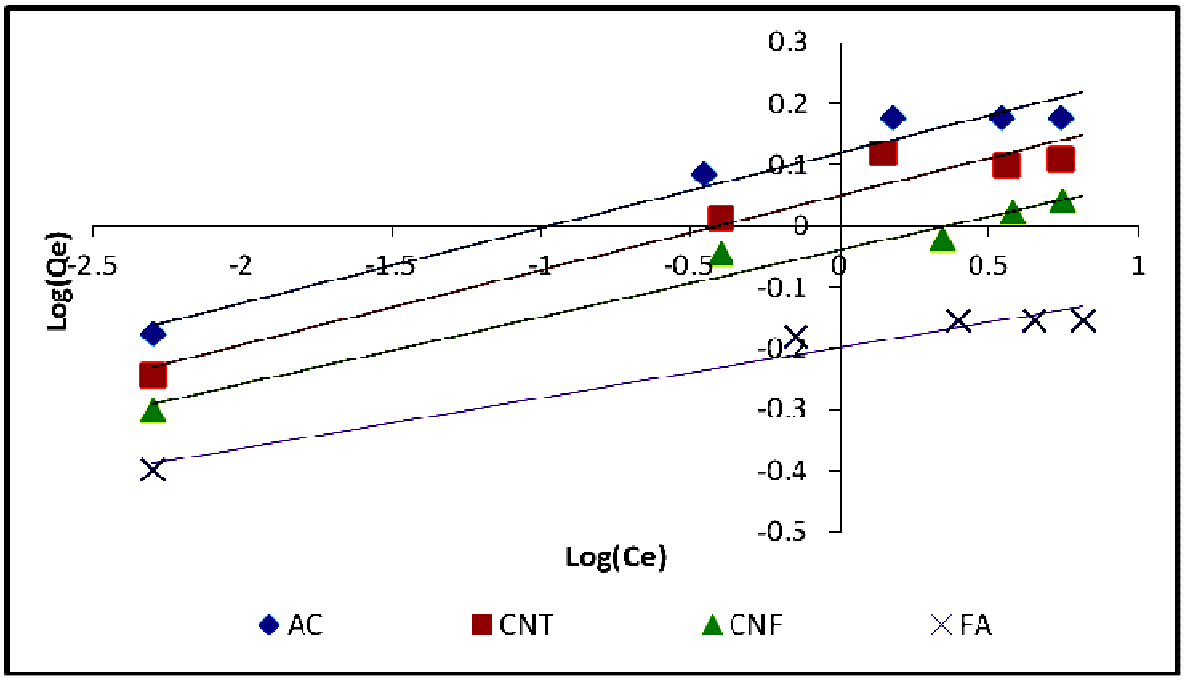


Figure 4-55 : Freundlich Adsorption isotherm model for 4-CP at pH6 raw CBAs

From Figures 4-54 and 4-55, the maximum adsorption capacities and the interceptions of the adsorbents were obtained and reported in Table 4-3. From the data in this table, it is clear that the adsorption capacity for AC is the highest while FA took the lowest value of the raw adsorbents, CNTs and CNFs has medium adsorption capacity.

Table 4-3 : Langmuir and Freundlich Isotherm Parameters for 4-CP by raw CBAs

	Langmuir			Freundlich		
Adsorbent	Q_m(mg/g)	K_L (L/mg)	R^2	n	K_F	R^2
AC	1.5106	33.100	0.999	8.1967	1.3152	0.966
CNTs	1.2887	29.846	0.999	8.2645	1.1194	0.955
FA	0.7027	54.731	1.000	12.345	0.6324	0.962
CNFs	1.136	9.777	0.990	9.1743	0.9162	0.975

By compression between Langmuir and Freundlich isotherms from Figures 4-54 and 4-55, Langmuir isotherms shows better fitting for the adsorbents with excellent correlation coefficients (specially for FA). On the other hand, Freundlich showed an acceptable fitting to the observational data with a good correlation coefficient.

The Langmuir and Freundlich equation were also used to describe the data derived from the adsorption of 4-Chlorophenol by modified carbon based adsorbents with aluminum. The adsorption capacity and the intensities were determined from the slope and intercept for each adsorbent from Figures 4-56 and 4-57.

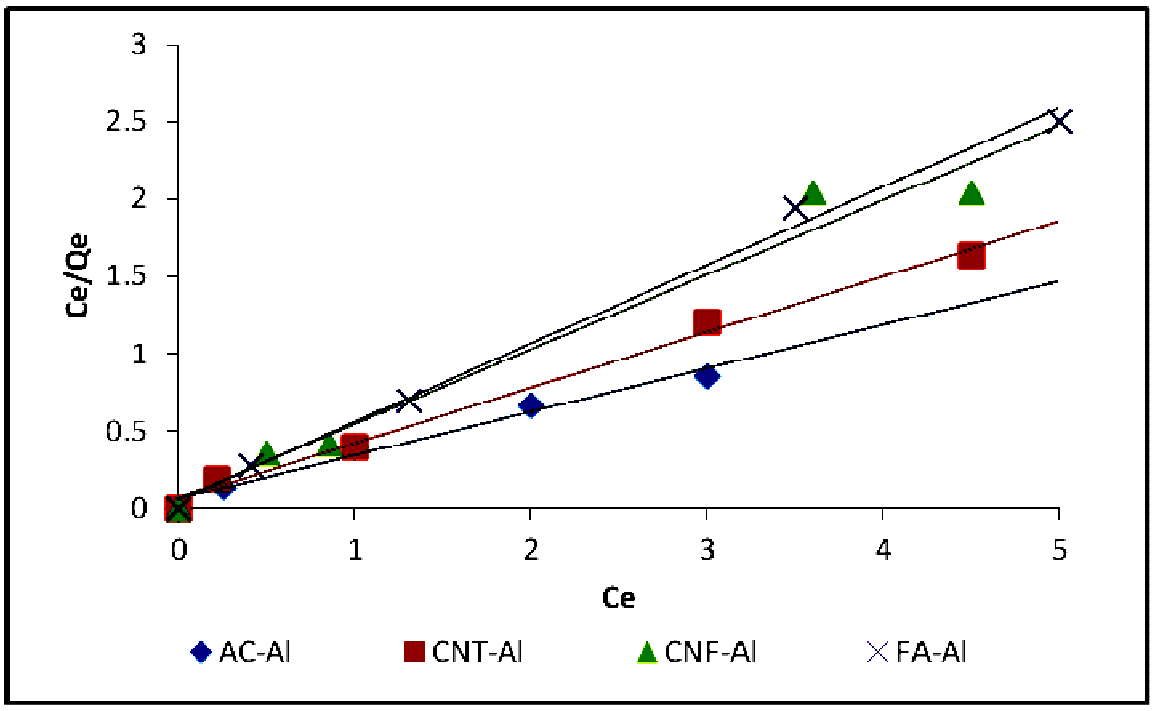


Figure 4-56 : Langmuir Adsorption isotherm model for 4-CP at pH 6 by MCBAs

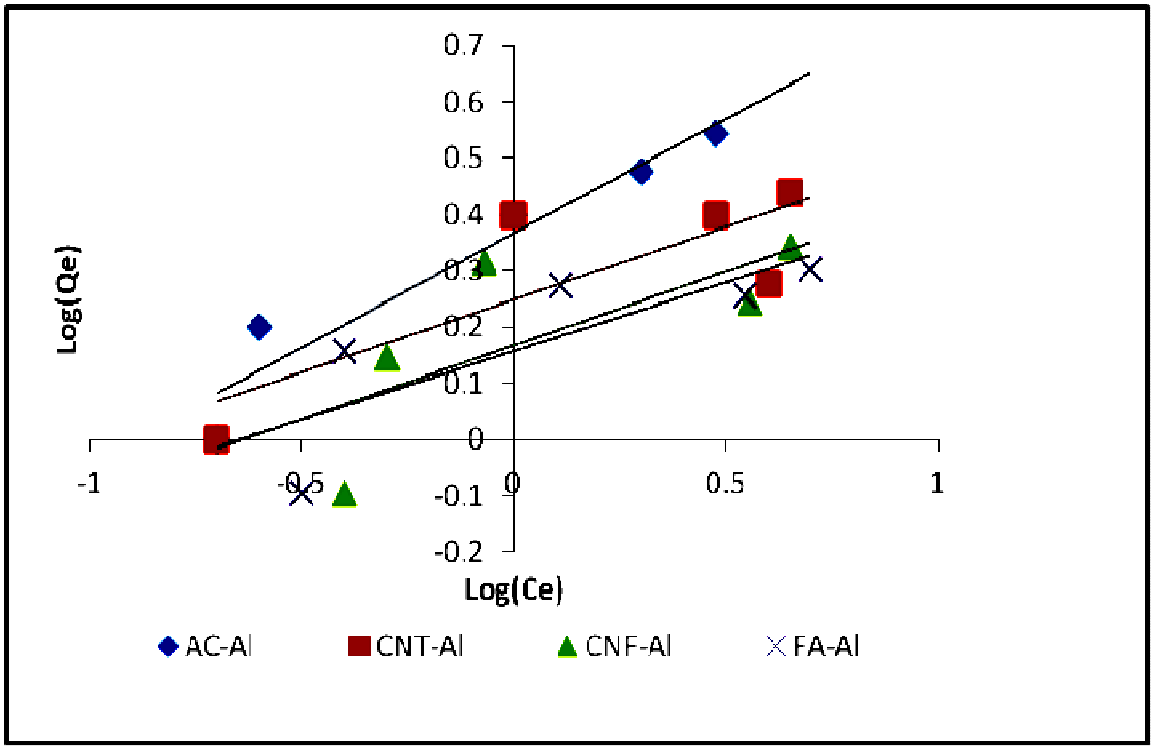


Figure 4-57 : Freundlich Adsorption isotherm model for 4-CP at pH6 by MCBAs

From Figure 4-56, Langmuir isotherms showed better fitting to the experimental data with good correlation coefficients. On the other hand, the Freundlich isotherm model from Figure 4-57, showed a poor fitting to the data by CBAs modified by aluminum. Table 4-4 showed the adsorption capacity of the modified adsorbents and their correlation coefficient.

Table 4-4 : Langmuir and Freundlich Isotherm Parameters for 4-CP by MCBAs

	Langmuir			Freundlich		
Adsorbent	Q_m(mg/g)	K_L (L/mg)	R^2	n	K_F	R^2
AC-Al	3.5461	4.8621	0.978	2.322	2.5823	0.928
CNTs-Al	2.7778	6.545	0.994	3.906	1.774	0.660
FA-Al	1.9763	10.542	0.994	4.1152	4.4668	0.650
CNFs-Al	2.0661	8.6429	0.973	4.1152	4.4667	0.650

As shown in Table 4-4, the adsorption capacity values for CBAs modified by aluminum indicate effective efficiency in their removal of 4-Chlorophenol. By comparing between this modified adsorbents, we found that the AC -Al took the highest value among all other modified adsorbent. The CNT-Al and CNF-Al showed good values of adsorption capacity but less than the AC-Al, while FA-Al ranking lastly between all modified adsorbents.

4.4 Modeling of kinetic Adsorption

The study of the kinetic modeling is the most important especially in the industrial application of adsorption. It offers good information for making comparison among various materials under different operation conditions to get optimal design operation condition for treatment of water and wastewater systems.

The kinetic for phenol and 4-Chlorophenol were investigated using the experimental data obtained from the effect of the adsorbents dosage rate at room temperature ($22^{o}C$) at several different time intervals up to 120 min. The kinetic of the adsorption was described by first order, second order and the pseudo –second order rate equation as follows:

The first order rate equation:

$$Log\frac{Q_e - Q_t}{Q_e} = -\frac{K_L\ t}{2.303} \text{----------(4.1)}$$

The estimated quantity of log (Q_e-Q_t) well plotted versus (t).

The second order rate equation is expressed by:

$$\frac{1}{Q_e - Q_t} = \frac{1}{Q_e} + K_2 t \text{----------(4.2)}$$

The values of Q_e and K_2 were obtained from the slope and the intercept of plotting (t) versus ($1/(Q_e$-$Q_t)$

The pseudo –second order rate equation according to McKay [89] was expressed by:

$$\frac{t}{Q_t} = \frac{1}{2K_s Q_e^2} + \frac{t}{Q_e} \text{----------(4-3)}$$

The values of Q_e and K_s were obtained from the slope and intercept of plotting t versus t/Q_t

4.4.1 Kinetics Adsorption Model of Phenol

The first and second order equations were plotted in Figures (4-58 and 4-59) for the phenol removal by using raw adsorbents.

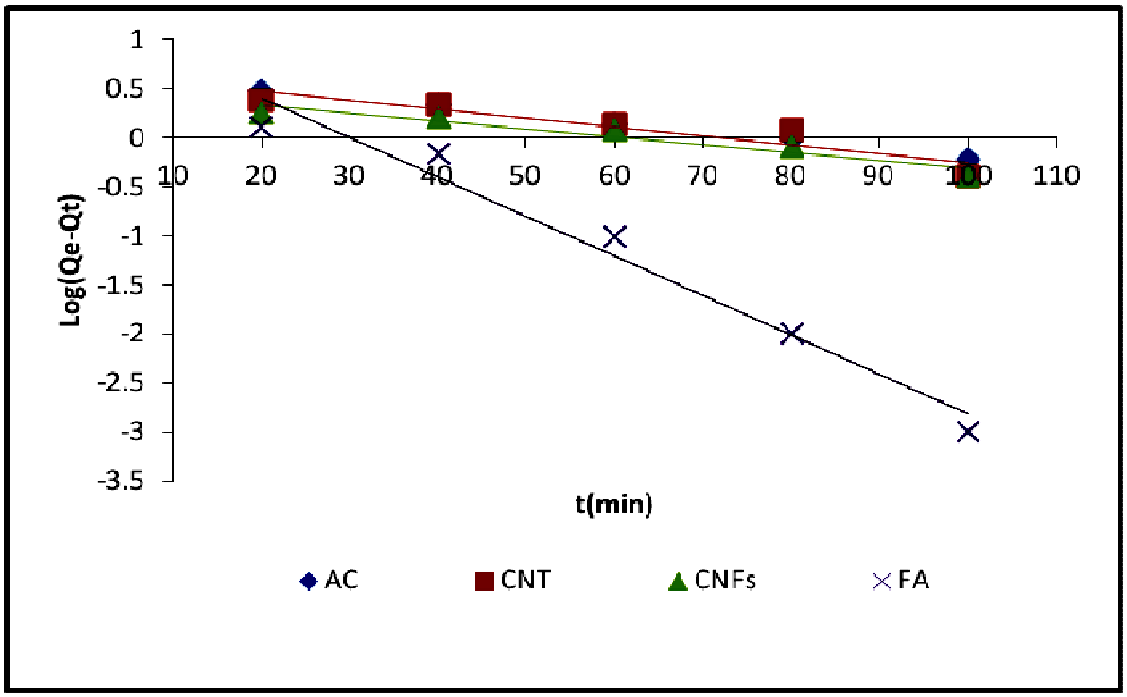


Figure 4-58 : First orders kinetic Model for removal phenol (2ppm) by raw CBAs

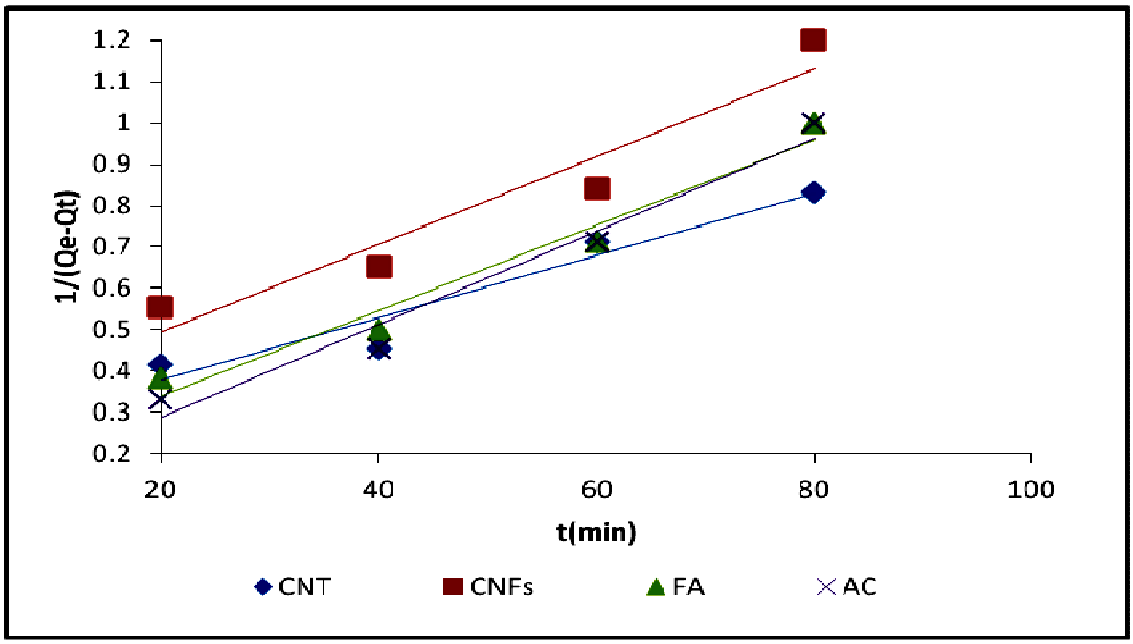


Figure 4-59 : Second order kinetic model for remove phenol (2ppm) by raw CBAs

The correlation coefficients for first and second order, was obtained from Figures (4-58 and 4- 59) respectively and reported in Table 4-5

Table 4-5 : Correlation Coefficients for kinetic Models of Phenol by raw CBAs

Adsorbent (50mg)	First Order	Second order
AC	0.993	0.971
CNT	0.855	0.933
CNF	0.921	0.928
FA	0.967	0.966

As shown in this Table the value of R^2 is the smallest for the first order kinetic equation for (CNT, CNF) compare with their R^2 of the second order kinetic equation. Thus, the second order equation was used in this study to investigate the adsorption mechanism of the 4-Chlorophenol by the raw (CNT, CNF).

Then again, as clear from Table 4-5, the R^2 for (AC and FA) is higher in the first order kinetic model than in the second order kinetic model, hence the first order was used to describe the removal of phenol by raw AC and FA.

So, the kinetic parameters for first order for phenol at pH 7 were obtained from Figure 4.58 and reported in Table 4-6 for AC and FA, while the parameters for second order for phenol at pH 7 were obtained from Figure 4-59 and reported in Table 4-7 for CNT and CNF, respectively.

Table 4-6 : Kinetic Parameter for First order Model of Phenol by raw AC &FA

Adsorbent (50mg)	Q_e (mg/g)	K_1 (min^{-1})	R^2
AC	4.6774	0.018424	0.993
FA	16.3305	0.09212	0.967

Table 4-7 : Kinetic Parameter for Second order Model of Phenol by raw CNT&CNF

Adsorbent (50mg)	Q_e (mg/g)	$K_2(min^{-1})$	R^2
CNT	4.3859	0.007	0.933
CNF	3.5587	0.010	0.928

Similar to the suitable kinetic model of removal phenol by modified adsorbents, the correlation coefficients for the first order, second order and Pseudo-second order equation are compared in Table 4-8.

Table 4-8 : Correlation Coefficients for kinetic Models of Phenol by MCBAs

Adsorbent (50mg)	First Order	Second Order	Pseudo –second order
AC-Al	***0.998***	0.940	0.997
CNT-Al	0.950	0.708	**0.982**
CNF-Al	**0.966**	0.880	0.857
FA-Al	0.734	0.500	**0.939**

As indicated in Table 4-8, the first order equation was used in this study to investigate the adsorption mechanism of the phenol by the modified (AC and CNF), while the pseudo –second order kinetic model was used to describe the removal by (CNT and FA) as shown in Figure 4-60 and Figure 4-61, respectively.

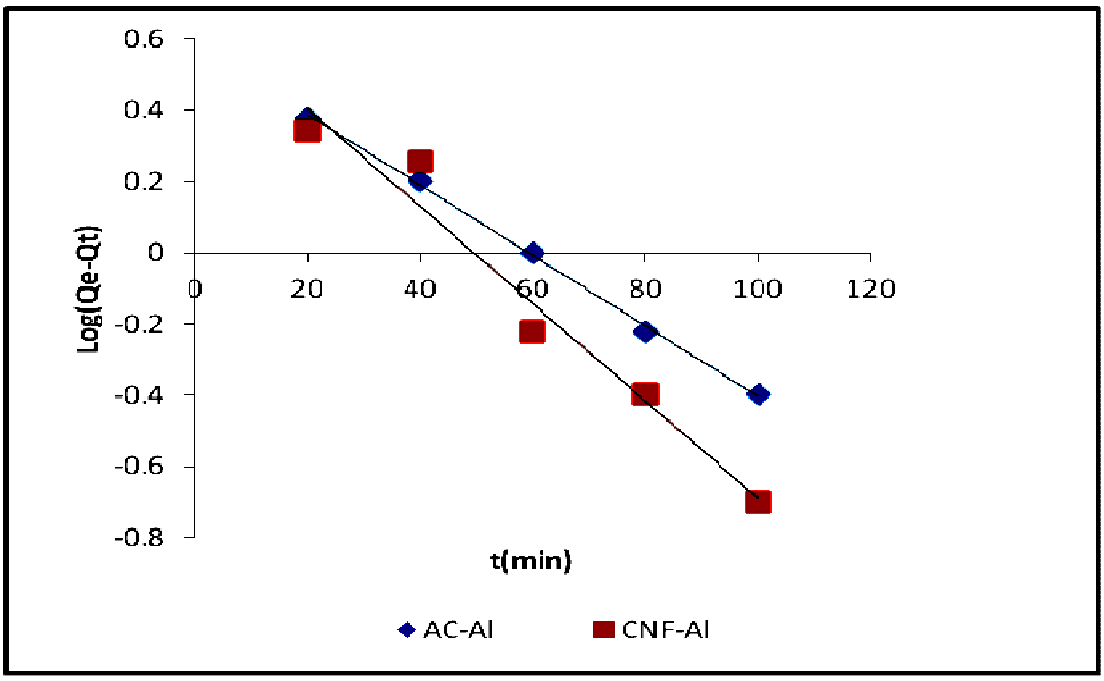


Figure 4-60 : First orders kinetic Model for removal phenol (2ppm) by MAC and MCNFs

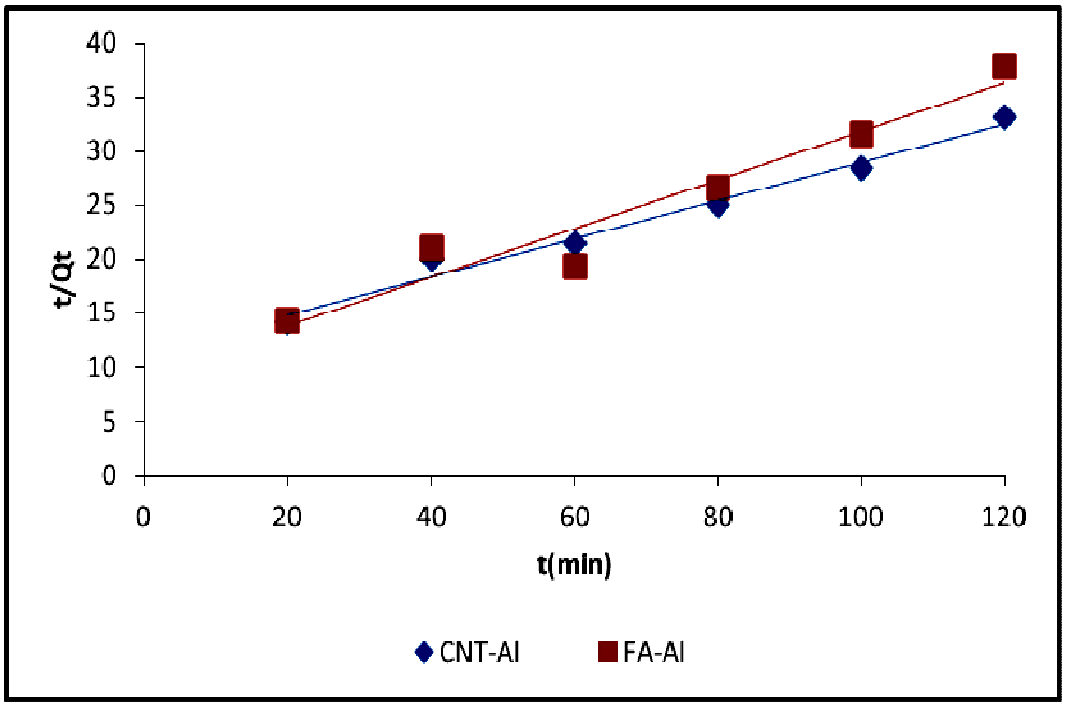


Figure 4-61 : Pseudo- Second order kinetic model for remove phenol (2ppm) by MCNT and MFA

Figures 4-60 and 4-61 were used to obtain the first and pseudo-second order kinetic parameter model for phenol at pH7 and reported in Table 4-9 for (AC-Al, CNF-Al), and Table 4-10 for (CNT-Al, FA-Al), respectively.

Table 4-9 : Kinetic Parameter for first order Model of Phenol

Adsorbent (50mg)	Q_e (mg/g)	$K_L(min^{-1})$	R^2
AC-Al	3.863	0.0207	0.998
CNF-Al	4.732	0.0299	0.966

Table 4-10: Kinetic Parameter for Pseudo- second order Model of Phenol

Adsorbent (50mg)	Q_e (mg/g)	$K_S(g\text{-}mg^{-1}.min^{-1})$	R^2
CNT-Al	5.6818	0.00136	0.982
FA-Al	4.8309	0.00190	0.847

The equilibrium adsorption capacity (Q_e) obtained in Tables (4-9 and 4-10), implies that the modified CNTs and modified CNF has higher adsorption capacities than the raw CNTs and CNFs, which show the great force of the modification on this two adsorbents. On the other hand, the modification of the AC and FA has a low effect on their adsorption capacities, but still AC has a high removal of phenol due to its special pore structure.

4.4.2 Kinetic Adsorption Model of 4-Chlorophenol

The first order equation and second order model were used to describe the kinetic adsorption of the 4-chlorophenol on the raw based carbon adsorbents as shown in Figures 4-62 and 4-63. The correlation coefficient for each model were obtained and reported in Table 4-11.

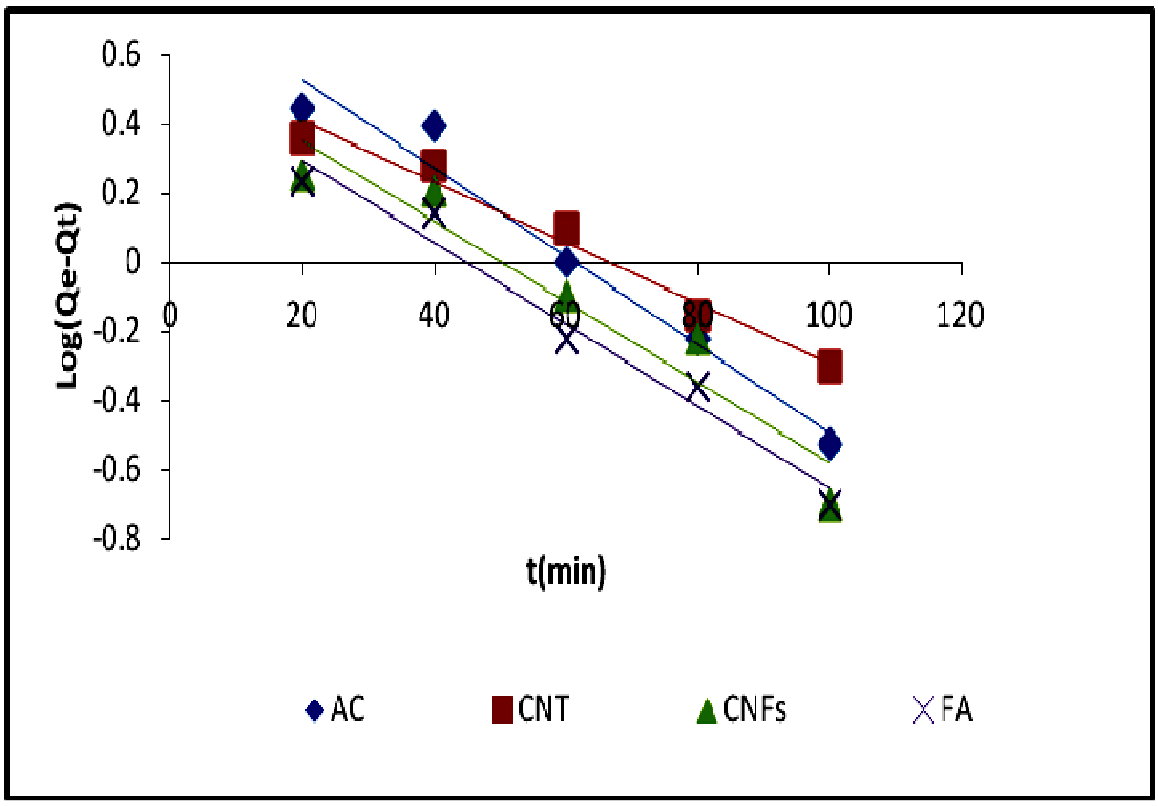


Figure 4-62 : First orders kinetic Model for removal 4-CP by raw CBAs

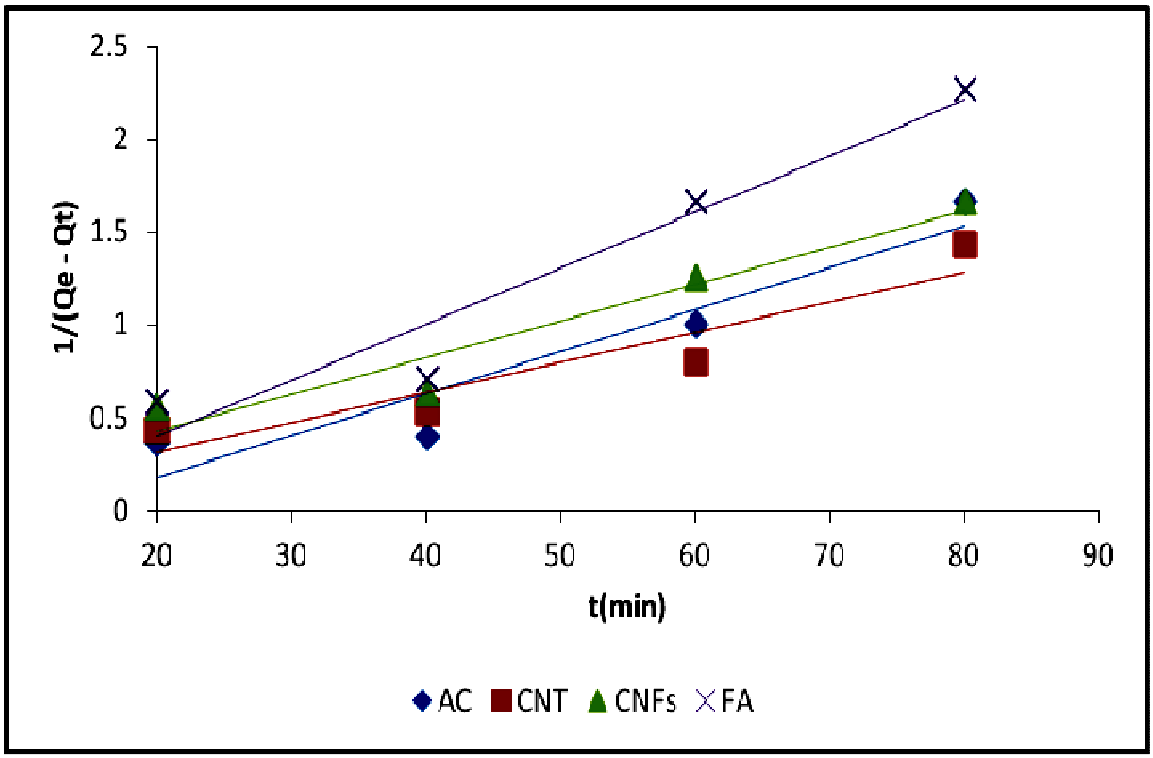


Figure 4-63 : Second orders kinetic Model for removal 4-CP by raw CBAs

Table 4-11: Correlation Coefficients for kinetic Models of 4-CP by raw CBAs

Adsorbent (50mg)	First Order	Second Order
AC	0.965	0.903
CNT	0.976	0.874
CNF	0.921	0.920
FA	0.967	0.935

As clear from Table 4-11, the first order model gave better correlation coefficient than a second order model, hence the first order was chosen to describe the adsorption of the observational data and its kinetic parameters are indicated in Table 4-12

Table 4-12: Kinetic Parameter for First order Model of 4-CP by raw CBAs

Adsorbent (50mg)	Q_e (mg/g)	$K_L(min^{-1})$	R^2
AC	6.123	0.02764	0.965
CNT	3.837	0.01842	0.976
FA	3.4041	0.02533	0.967
CNF	3.8725	0.02533	0.921

Likewise, the first order equation was found to have the best fit to describe adsorption kinetic of the modified carbon based adsorbents with a high correlation coefficient as shown in Figure 4-64.

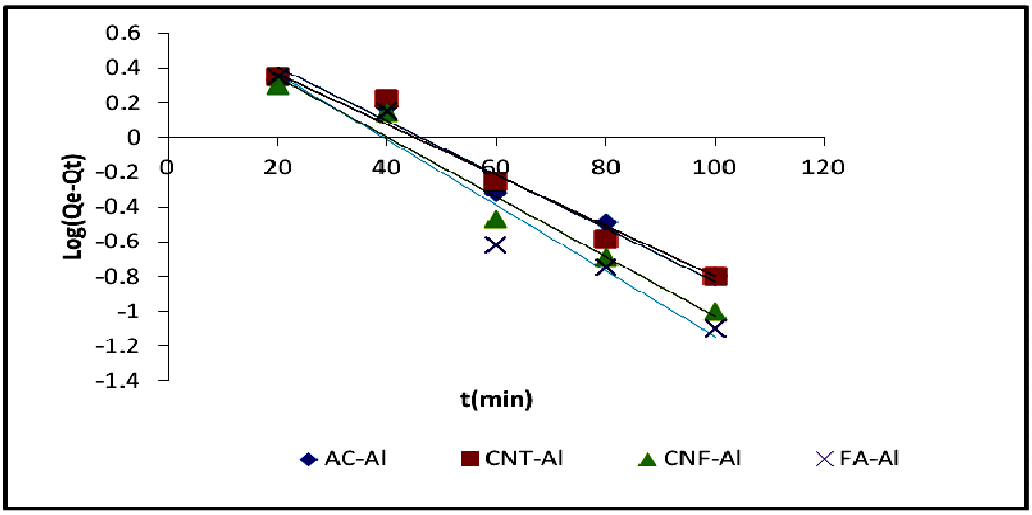


Figure 4-64 : First Orders kinetic Model for removal 4-CP by MCBAs

The constant parameter for the first order kinetic adsorption model for 4-chlorophenol by the modified adsorbent was shown in Table 4-13.

Table 4-13: Kinetic Parameters for First order Model of 4-CP by MCBAs

Adsorbent (50mg)	Q_e (mg/g)	$K_L(min^{-1})$	R^2
AC-Al	4.5394	0.0322	0.973
CNT-Al	5.199	0.0345	0.975
CNF-Al	4.8978	0.0392	0.967
FA-Al	5.546	0.0414	0.945

The effect of modification on the CNT, CNF recovered a great effect on the adsorption capacities of these adsorbent. The modifications lead to increase in the adsorption capacities of these nano adsorbents materials. As example, the adsorption capacity of raw CNT were found to be 3.837 (mg/g), while in the modified form (CNT-Al), it reached 5.2 (mg/g). Similar behavior was noticed for the CNF, the adsorption capacity for the raw CNF was found to be 3.8 (mg/g), while in the modified form (CNF-Al), it reached 4.89 (mg/g). From these result, we can conclude that the impregnation of metals on the

nano carbon materials (CNT and CNF) has a great affect on the enhancement of the adsorption capacity than the micro carbon materials (AC &FA).

4.5 Comparative Analysis of Various Adsorbents for Phenol and 4-Chlorophenol removal

In this section, we reported some of the updated works that have been performed to remove phenolic compounds from water by using different adsorbents Table 4-14

Table 4-14: Comparison of various adsorbents and their uptake of Phenol

Adsorbents	Adsorbate	Solution volume (ml)	Con (mg/l)	pH	Q_m(mg/g)	Reference
AC	Phenol	50	1.0	6.0	1.20	[90]
CAC	Phenol	10	10	3.4	6.8	[79]
SACFA	Phenol	30	20	2.22	0.284	[82]
FA	Phenol	50	10	6.5	9.498	
ACC	Phenol	50	10	6.5	7.068	[92]
AC	Phenol	100	2	7	1.3477	This work
AC-Al	Phenol	100	2	7	3.174	
FA	Phenol	100	2	7	1.007	
FA-Al	Phenol	100	2	7	2.105	
CNTs	Phenol	100	2	7	1.0977	
CNTs-Al	Phenol	100	2	7	2.000	
CNFs	Phenol	100	2	7	0.8418	
CNFs-AL	Phenol	100	2	7	1.684	

SACFA : South Africa Coal Fly Ash

ACC : Activated Carbon Commercial grade

Table 4-15: Comparison of various adsorbents and their uptake of 4-CP

Adsorbents	Adsorbate	Solution volume(ml)	Con(mg/l)	pH	Q_m(mg/g)	Reference
AC	4-CP	50	1.0	6.0	1.28	[90]
MCNT	4-CP	50	1.0	6.8	1.30	[94]
AC	4-CP	100	2	6.0	1.5106	This work
AC-Al	4-CP	100	2	6.0	3.546	
CNT	4-CP	100	2	6.0	1.2887	
CNT-Al	4-CP	100	2	6.0	2.778	
CNF	4-CP	100	2	6.0	1.136	
CNF-Al	4-CP	100	2	6.0	2.0661	
FA	4-CP	100	2	6.0	0.7027	
FA-Al	4-CP	100	2	6.0	1.9763	

As shown in Tables 4-14 and 4-15, there are few studies that have been conducted on the removal of phenol and 4-chlorophenol using CNTs and CNFs. The maximum adsorption capacity for each adsorbents is different from each other due to the fluctuation in the operation condition (pH, contact time, agitation speed, temperature, dosage rate, solution volume and many more) Thus, this comparative study was conducted to understand the mechanism of adsorption and to compare the various adsorbents that were used to remove phenol and 4-Chlorophenol.

In 2004, Sumol [90] used activated carbon to treat water from phenol and 4-Chlorophenol with concentration of 1ppm in 50ml. The solution maximum adsorption capacity (Q_m) was 1.20, 1.28 mg/g at pH 6, respectively. In comparison with Riaz Qadeer [79] who used commercial activated carbon to remove phenol with 10 ppm concentration in 10 ml at pH 3.4, he got Q_m= 6.8 mg/g. While in 2007, Samson [82] studied the removal of

phenol by Fly ash obtain from South Africa (Coal FA).He used concentration of 20 ppm in 30 ml volmitric flask at pH 2.22, the maximum adsorption capacity that he found was Q_m= 0.284 mg/g. In 2005, Vimal C. Srivastava[92] used baggase fly ash and commercial activated carbon to remove phenol with 10 ppm in 50 ml volumetric flask at pH of 6.5, he found that Q_m= 9.498 for FA and 7.068 mg/g for AC.

In 2010, M Abdel Salam [94] used MCNTs as new adsorbent to treat 4-Chlorophenol from water. He used concentration of 1 ppm in 50 ml volumetric flask at pH 6.8, the maximum adsorption capacity he achieved was 1.30 (mg/g).

Finally, in this study we have succeeded to get good adsorption capacities to all adsorbents based carbon impregnated with aluminum oxide except for raw CNFs which recover low adsorption for phenol (Table 4-14), especially we used high volume of stock solution which is 100 ml. The maximum adsorption capacity for phenol with 2 ppm concentration in100 ml volumetric flask at pH 7 is 3.1, 2.1, 2.0 and 1.6 (mg/g) for modified AC, FA, CNTs and CNFs with aluminum, respectively. On the other hand, the maximum adsorption capacity of 4- Chlorophenl with 2 ppm concentration in 100 ml volumetric flack at pH 6.0 is 3.5, 1.90, 2.7 and 2.06 (mg/g) for modified AC, FA, CNTs and CNFs with aluminum(see Table 4-15), respectively.

CHAPTER 5

CONCLUTION AND RECOMMENDATIONS

Carbonic materials were found effective for the adsorption of phenol and 4-Chlorophenol from aqueous solution. The characterization of phenol uptake showed that, the phenol molecules binding depends on initial pH, agitation speed, contact time and dosage of adsorbents.

The removal percentage increased with the increase in pH from pH 3 to pH 7 then decreased from pH 7 to pH 9. The maximum removal observed in this study was at pH 7 (for both regular and modified forms for all adsorbents) in which it gave approximately 47%, 42% and 30% removal of phenol molecules by using regular CNT, FA and CNF, respectively, whereas the AC showed a removal close to 65%. This percentage of removal was increased significantly up to 83%, 84% and 86% for modified form of AC with Ti, Fe and Al. The modified form of the CNT, CNF and FA with Al, enhanced the removal of phenol up to 76%, 75% and 75%, respectively.

In addition, phenol removal was increased slightly with the increase in the shacking speed from 50 to 200 rpm, from which 200 rpm gave higher removal for phenol by regular and modified forms of adsorbents. The percentage removal increased sharply with the increase in time until it reaches the maximum after 2 hours, by using both regular and modified forms of adsorbents. Moreover, it was observed that the removal percentage was increased with the increase in dosage rate until it reaches 100% removal by using 0.3, 0.4, 0.5 and 0.6 g for regular AC, CNT, FA and CNF, respectively. Whereas we found 100 % removal was achieved by using 0. 2, 0.25, 0.15 and 0.2 g of modified AC, CNT, FA and CNF with aluminum, respectively. Dosage less than 50 mg was found to be not effective on the phenol removal.

From these results, it was noticed that the effect of the impregnation of metals, like Al on the nano carbonic materials such as CNFs is greater in the enhancement of the

adsorption mechanism than in micro carbonic material like AC (although the removal of the AC is always higher than the CNF).While 0.3 g of AC is needed to achieved 100% removal, only 0.2 g is needed when AC-Al is used, which is 33 % lower in the dosage. The same can also be noticed for CNF when compared with CNF-Al. In this case 66 % lower dosage is needed to achieve 100 % removal. By fixing the operation condition at pH 7, 2 hours contact time, 200 rpm shacking speed and 0.1 g rate dosage, the efficiency of phenol removal reached up to 95%, 92%, 91% and 89% by using modified form of AC, CNT, FA and CNFs with Al, respectively.

The characterization of 4-chlorophenol uptake showed that, the 4-Chlorophenol molecular binding depends on the initial pH, agitation speed, contact time and dosage of adsorbents. Removal percentage increased with the increased in the pH from pH 3 to pH 6, then decreased in the range of pH 6 to pH 8. The maximum removal of 4-Chlorophenol observed in this study at pH 6 (for both regular and modified forms for all adsorbents). This removal reached up to 52%, 32 % and 37% by using regular CNT, FA and CNF, respectively. The AC showed a removal close to 62 %, this percentage of removal was increased significantly to 64%, 74% and 77% for modified form of AC with Fe, Ti and Al, respectively.

The modified form of the CNT, CNF and FA with Al, enhanced the removal of 4-chlorophenol to 77%, 76 % and 73%, respectively. Moreover, the percentage removal increased slightly with the increase in the shacking speed from 50 to 150 rpm, in which 150 rpm gave approximately higher removal for 4-chlorophenol for both regular and modified forms of adsorbents. The percentage of the removal increased sharply with the increase in the contact time and it reached the maximum after 2 hours followed by equilibrium state in removal beyond 2 hours for both regular and modified forms of adsorbents.

Moreover, it was observed that the removal percentage increased with the increase in dosage rate until reaching 100% removal by using 0.3, 0.40, 0.5 and 0.4 g of regular AC, CNT, FA and CNF, respectively. Whereas we found 100 % removal was achieved by using 0.2, 0.2, 0.3 and 0.2 g of AC-Al, CNT-Al, FA-Al and CNF-Al, respectively. Similar to the phenol, the dosage less than 50 mg was found to be not

effective on the removal efficiency for 4-chlorophenol. However, by fixing the operation condition at pH6, 2 hours contact time, 150 rpm shacking speed and 0.1g rate dosage, the efficiency of the removal of 4-chlorophenol can reached up to 93.4 %, 89.3 %, 86.2 % and 82.7 % by using modified form of AC, CNT, CNF and FA with Al, respectively.

Impregnation of metals such as aluminum, titanium and iron were found to be very effective for the removal of both phenol and 4-chlorophenol from aqueous solution. The adsorption of regular forms of carbonic materials is a physical process depending on the van der Waals' forces. The adsorption occurred due to fact that the attraction forces between the phenol and 4-chlorophenol (solutes) and adsorbents were greater than the forces attraction between the phenol and 4-chlorophenol (solutes) and the water solution (solvent). The modification form of this carbonic material is particularly physical due to the increase in the surface area of the adsorbents by the metals, and other part could be chemical which is due to the formation of the metal oxides on the adsorbents surfaces.

The three carbonic adsorbent materials, regular AC, MAC and MCNT have the highest removal ability for phenol and 4-chlorophenol and can be considered to be good adsorbents in the water treatment application. Regular, CNT, CNF and FA are also good but with high dosage rate, whereas MCNF and FA are also good for water treatment with average dosage rate.

From the above analysis, it was shown that the modified AC, CNT, CNF, and FA with metal oxide can be used as adsorbents for phenol and 4-chlorophenol removal from water and waste water treatment, but more study must be done to demonstrate the other aspects of this method, such as the costs and the treatment of phenol and 4-chlorophenol in large scale in real life.

The maximum adsorption capacity for AC and CNT in their modified form were found to be very excellent for both phenol and 4-Chlorophenol adsorption. On the other hand, the maximum adsorption capacity for both modified FA and CNF showed average value for both phenol and 4-Chlorophenol adsorption.

Lastly , in this study it was shown that the adsorption for these four adsorbents in their regular and modification forms can be understood by both Langmuir and Freundlich and obtain good adsorption capacity for phenol and 4-chlorophenol. Moreover, the kinetic adsorption of phenol by raw micro CBAs (AC and FA) is represented better by first order, whereas the nano CBAs (CNT and CNF) is represented better by second order. The modified form of AC and CNF (AC-Al and CNF-Al) was found better represented by first order, the best representation of CNT-Al and FA-Al founded by the second order.

4-chlorophenol by regular adsorbents is represented better by both first order and second order, whereas the modified form of this CBAs represented best by the first order kinetic model.

Recommendation

From this study I recommend to:

- Introduce FA as good adsorbents in the water treatment fields .Fly ash is good potential adsorbent that is inexpensive and readily available in Saudi Arabia and could be utilized to remove other organic compounds.
- Explore the impregnation of other metals such as silver and copper to treat water from organic pollutants such as benzene and toluene.

This study must conduct the:

1. Purification of the carbon based adsorbents should be performed to obtain the greatest purity of these adsorbents.
2. Hazard of using adsorbents especially CNTs and CNFs on the human health should be studied thoroughly in order to protect human body.
3. The effect of the presence of other metals such as silver and nickel in the FA on the treatment process should be studied.

4. Real water that is polluted with both phenol and 4-Chlorophenol from the selected groundwater in the area of oil field should be used to study the effectiveness of these modified adsorbents on the actual wastewater.

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APPENDIXES

APPENDIX A

EXPERMENTAL RESULTS FOR

Table A.1 Phenol removal % by Activated Carbon

	Time	Dosage	Agitation speed	AC	AC-Al	AC-Ti	AC-Fe
pH	(hr)	(mg)	(rpm)	Removal %	Removal %	Removal %	Removal %
3	2	50	100	25.5	65.4	63.3	63.3
4	2	50	100	36.1	72.7	69.6	70.6
5	2	50	100	45.7	76.4	73.2	75.3
6	2	50	100	59.5	82.1	81.1	82.1
7	2	50	100	64.8	85.3	83.7	84.2
8	2	50	100	54.2	74.8	74.8	73.8
9	2	50	100	30.8	-	-	-

Agitation Speed	Time	Dosage	pH	AC	AC- Al	AC-Ti	AC-Fe
rpm	(min)	(mg)		Removal %	Removal %	Removal %	Removal %
50	120	50	7	44.6	76.4	73.8	73.8
100	120	50	7	64.8	85.3	83.2	84.2
150	120	50	7	73.4	92.1	89.5	90.5
200	120	50	7	74.4	92.1	89.5	89.5
250	120	50	7	74.46	-	-	-

Time	Agitation Speed	Dosage	pH	AC	AC- Al	AC-Ti	AC-Fe
min	rpm	(mg)		Removal %	Removal %	Removal %	Removal %
10	200	50	7	2.65	36.6	31.9	33.5
30	200	50	7	14.8	52.3	43.4	49.7
60	200	50	7	48.9	79.0	76.4	79.0
120	200	50	7	74.4	93.1	89.5	90.5
240	200	50	7	67.0	83.76	84.8	85.8
720	200	50	7	48.9	78.0	75.3	80.1

Dosage	Agitation Speed	Time	pH	AC	AC-Al	AC-Ti	AC-Fe
mg	rpm	min		Removal %	Removal %	Removal %	Removal %
10	200	120	7	24.4	68.5	63.3	65.4
50	200	120	7	74.4	93.7	89.5	90.5
100	200	120	7	80.8	94.7	92.1	93.1
200	200	120	7	89.3	100	100	100
250	200	120	7	94.6	100	100	100
300	200	120	7	100	100	100	100

Table A.2 Phenol removal % by CNTs

	Time	Dosage	Agitation speed	CNT	CNT-Al	CNT-Ti	CNT-Fe
pH	(min)	(mg)	(rpm)	Removal %	Removal %	Removal %	Removal %
3	120	50	100	6.3	56.0	54.9	54.9
4	120	50	100	25.5	67.5	62.3	63.8
5	120	50	100	35.1	73.8	68.5	71.7
6	120	50	100	41.4	74.8	73.8	72.7
7	120	50	100	46.8	76.4	73.8	74.8
8	120	50	100	42.5	73.2	72.7	73.8
9	120	50	100	20.2	-	-	-

Agitation Speed	Time	Dosage	pH	CNT	CNT-Al	CNT-Ti	CNT-Fe
rpm	(min)	(mg)		Removal %	Removal %	Removal %	Removal %
50	120	50	7	29.7	67.5	65.4	66.4
100	120	50	7	46.8	76.4	73.8	74.8
150	120	50	7	61.7	90.5	83.2	86.3
200	120	50	7	62.7	90.0	83.7	86.3
250	120	50	7	62.7	90.1	83.6	86.3

Time	Agitation Speed	Dosage	pH	CNT	CNT-Al	CNT-Ti	CNT-Fe
min	rpm	(mg)		Removal %	Removal %	Removal %	Removal %
10	200	50	7	1.0	37.1	31.9	32.4
30	200	50	7	9.0	48.1	41.8	47.6
60	200	50	7	26.5	73.8	67.5	70.1
120	200	50	7	62.7	90.5	83.2	86.3
240	200	50	7	61.7	83.2	81.6	83.2
720	200	50	7	46.8	81.1	72.7	80.6

Dosage	Agitation Speed	Time	pH	CNT	CNT-Al	CNT-Ti	CNT-Fe
mg	rpm	min		Removal %	Removal %	Removal %	Removal %
10	200	120	7	18.0	65.9	59.6	64.3
50	200	120	7	62.7	90.5	83.7	86.3
100	200	120	7	75.5	92.1	88.5	89.5
150	200	120	7	78.9	96.8	94.7	95.2
200	200	120	7	82.4	99.1	98.9	99.4
250	200	120	7	86.9	100	100	100
300	200	120	7	91.4	100	100	100
400	200	120	7	100	100	100	100
450	200	120	7	100	100	100	100

Table A.3 Phenol removal % by raw and Modified CNFs

	Time	Dosage	Agitation speed	CNF	CNF-Al	CNF-Ti	CNF-Fe
pH	(min)	(mg)	(rpm)	Removal %	Removal %	Removal %	Removal %
3	120	50	100	4.2	54.9	50.2	53.4
4	120	50	100	9.5	66.4	55.4	58.6
5	120	50	100	14.8	71.7	60.7	68.5
6	120	50	100	25.5	74.3	69.1	71.2
7	120	50	100	30.8	75.9	70.1	72.2
8	120	50	100	25.5	69.1	60.7	65.9
9	120	50	100	17.0	-	-	-

Agitation Speed	Time	Dosage	pH	CNF	CNF-AL	CNF-Ti	CNF-Fe
rpm	(min)	(mg)		Removal %	Removal %	Removal %	Removal %
50	120	50	7	6.3	74.3	55.4	59.1
100	120	50	7	30.8	75.9	70.6	72.2
150	120	50	7	37.2	89.5	80.6	79.5
200	120	50	7	43.6	90.0	80.1	79.0
250	120	50	7	43.6	-	-	-

Time	Agitation Speed	Dosage	pH	CNF	CNF-Al	CNF-Ti	CNF-Fe
min	rpm	(mg)		Removal %	Removal %	Removal %	Removal %
10	200	50	7	0	32.4	23.5	25.1
30	200	50	7	3.1	47.1	34.5	36.1
60	200	50	7	14.8	74.3	52.3	53.9
120	200	50	7	43.6	89.5	80.1	79.0
240	200	50	7	41.4	83.2	74.3	78.5
720	200	50	7	36.1	76.9	69.1	72.7

Dosage	Agitation Speed	Time	pH	CNF	CNF-Al	CNF-Ti	CNF-Fe
mg	rpm	min		Removal %	Removal %	Removal %	Removal %
10	200	120	7	6.91	64.3	55.4	60.7
50	200	120	7	43.6	87.4	76.4	79.0
100	200	120	7	61.7	89.5	84.8	86.3
150	200	120	7	70.2	96.8	92.1	95.8
200	200	120	7	78.7	100	98.4	99.4
300	200	120	7	84.0	100	100	100
400	200	120	7	89.3	100	100	100
500	200	120	7	92.0	100	100	100
600	200	120	7	100	100	100	100

Table A.4 Phenol removal % by raw and Modified FA

	Time	Dosage	Agitation speed	FA	FA-Al	FA-Ti	FA-Fe
pH	(min)	(mg)	(rpm)	Removal %	Removal %	Removal %	Removal %
3	120	50	100	6.3	60.7	53.9	55.4
4	120	50	100	22.3	69.6	61.2	62.3
5	120	50	100	30.8	72.7	67.5	70.1
6	120	50	100	36.1	74.8	70.1	72.2
7	120	50	100	42.5	75.9	71.7	73.2
8	120	50	100	37.2	71.7	69.1	70.6
9	120	50	100	15.9	-	-	-

Agitation Speed	Time	Dosage	pH	FA	FA-Al	FA-Ti	FA-Fe
rpm	(min)	(mg)		Removal %	Removal %	Removal %	Removal %
50	120	50	7	20.2	65.9	60.7	62.3
100	120	50	7	42.5	75.9	71.7	72.7
150	120	50	7	55.3	90.5	80.6	80.6
200	120	50	7	61.7	90.0	80.1	80.1
250	120	50	7	61.7	-	-	-

Time	Agitation Speed	Dosage	pH	FA	FA-Al	FA-Ti	FA-Fe
min	rpm	(mg)		Removal %	Removal %	Removal %	Removal %
10	200	50	7	1.5	31.4	24.6	26.7
30	200	50	7	7.9	37.6	37.1	42.4
60	200	50	7	26.0	79.0	52.8	53.9
120	200	50	7	61.7	90.5	84.2	85.8
240	200	50	7	59.5	85.8	80.1	81.1
720	200	50	7	41.4	78.0	72.2	76.4

Dosage	Agitation Speed	Time	pH	FA	FA-Al	FA-Ti	FA-Fe
mg	rpm	min		Removal %	Removal %	Removal %	Removal %
10	200	120	7	14.8	65.4	58.1	63.3
50	200	120	7	61.7	90.5	84.2	85.3
100	200	120	7	70.2	91.6	87.4	89.0
150	200	120	7	75.0	100	95.2	98.9
200	200	120	7	80.8	100	100	100
300	200	120	7	89.3	100	100	100
400	200	120	7	96.8	100	100	100
500	200	120	7	100	100	100	100

Table A.5 4-Chlorophenol removal % by raw and Modified AC

	Time	Dosage	Agitation speed	AC	AC-Al	AC-Ti	AC-Fe
pH	(min)	(mg)	(rpm)	Removal %	Removal %	Removal %	Removal %
3	120	50	100	29.6	59.8	56.8	39.0
4	120	50	100	39.6	69.5	63.9	49.7
5	120	50	100	48.7	76.6	70.0	58.8
6	120	50	100	61.8	77.1	74.6	60.9
7	120	50	100	59.7	73.6	69.5	59.8
8	120	50	100	56.7	70.0	65.9	50.7

Agitation Speed	Time	Dosage	pH	AC	AC-Al	AC-Ti	AC-Fe
rpm	(min)	(mg)		Removal %	Removal %	Removal %	Removal %
50	120	50	6	47.7	69.5	67.5	56.3
100	120	50	6	61.8	77.1	74.6	60.9
150	120	50	6	75.8	83.2	81.7	64.9
200	120	50	6	75.3	83.2	81.7	64.9
250	120	50	6	75.8	-	-	-

Time	Agitation Speed	Dosage	pH	AC	AC-Al	AC-Ti	AC-Fe
min	rpm	(mg)		Removal %	Removal %	Removal %	Removal %
10	150	50	6	5.0	26.9	22.8	13.7
30	150	50	6	15.5	43.1	36.5	38.0
60	150	50	6	50.2	71.0	67.0	56.8
120	150	50	6	75.3	83.2	81.7	64.97
240	150	50	6	75.8	81.7	79.6	64.4
720	150	50	6	75.3	80.2	79.1	63.9

Dosage	Agitation Speed	Time	pH	AC	AC-Al	AC-Ti	AC-Fe
mg	rpm	min		Removal %	Removal %	Removal %	Removal %
10	150	120	6	29.6	61.9	53.2	37.0
50	150	120	6	75.3	83.2	81.7	64.9
100	150	120	6	82.9	93.4	89.3	84.2
200	150	120	6	90.4	100	97.9	91.3
300	150	120	6	100	100	100	97.4
400	150	120	6	100	100	100	100

Table A .6 4-Chlorophenol removal % by raw and Modified CNTs

	Time	Dosage	Agitation speed	CNT	CNT-Al	CNT-Ti	CNT-Fe
pH	(min)	(mg)	(rpm)	Removal %	Removal %	Removal %	Removal %
3	120	50	100	7.0	57.8	51.7	31.4
4	120	50	100	22.1	69.0	58.3	43.1
5	120	50	100	26.6	75.6	64.9	50.7
6	120	50	100	52.2	76.1	70.0	63.4
7	120	50	100	50.2	74.1	67.5	61.4
8	120	50	100	44.7	69.0	64.4	51.7

Agitation Speed	Time	Dosage	pH	CNT	CNT-Al	CNT-Ti	CNT-Fe
rpm	(min)	(mg)		Removal %	Removal %	Removal %	Removal %
50	120	50	6	32.1	67.0	59.8	49.7
100	120	50	6	52.2	76.1	70.0	63.4
150	120	50	6	64.8	81.2	79.1	61.4
200	120	50	6	65.3	81.7	77.6	79.1
250	120	50	6	64.3	-	-	-

Time	Agitation Speed	Dosage	pH	CNT	CNT-Al	CNT-Ti	CNT-Fe
min	rpm	(mg)		Removal %	Removal %	Removal %	Removal %
10	150	50	6	2.0	22.3	14.2	8.6
30	150	50	6	11.5	37.5	31.4	35.5
60	150	50	6	30.6	67.0	65.4	56.8
120	150	50	6	64.8	81.2	79.1	61.4
240	150	50	6	64.3	83.2	78.6	64.9
720	150	50	6	63.8	82.7	79.1	64.4

Dosage	Agitation Speed	Time	pH	CNT	CNT-Al	CNT-Ti	CNT-Fe
mg	rpm	min		Removal %	Removal %	Removal %	Removal %
10	150	120	6	21.6	54.8	50.7	21.8
50	150	120	6	64.8	81.2	79.1	61.4
100	150	120	6	77.8	89.3	88.3	84.2
150	150	120	6	80.8	96.4	94.4	90.3
200	150	120	6	83.9	100	98.4	96.9
250	150	120	6	88.4	100	100	100
300	150	120	6	92.9	100	100	100
350	150	120	6	96.4	100	100	100
400	150	120	6	100	100	100	100

Table A .7 4-Chlorophenol removal % by raw and Modified CNFs

	Time	Dosage	Agitation speed	CNF	CNF-Al	CNF-Ti	CNF-Fe
pH	(min)	(mg)	(rpm)	Removal %	Removal %	Removal %	Removal %
3	120	50	100	9.5	56.3	37.5	20.8
4	120	50	100	17.0	67.5	52.2	36.0
5	120	50	100	23.1	72.5	63.9	43.6
6	120	50	100	37.1	76.1	74.1	61.4
7	120	50	100	27.6	76.6	72.5	56.3
8	120	50	100	22.1	70.0	41.1	39.5

Agitation Speed	Time	Dosage	pH	CNF	CNF-Al	CNF-Ti	CNF-Fe
rpm	(min)	(mg)		Removal %	Removal %	Removal %	Removal %
50	120	50	6	13.5	57.3	56.8	38.5
100	120	50	6	37.1	69.0	67.5	61.4
150	120	50	6	50.2	77.6	76.1	71.0
200	120	50	6	50.7	77.1	76.6	71.5
250	120	50	6	50.2	-	-	-

Time	Agitation Speed	Dosage	pH	CNF	CNF-Al	CNF-Ti	CNF-Fe
min	rpm	(mg)		Removal %	Removal %	Removal %	Removal %
10	150	50	6	5.5	14.2	11.6	6.0
30	150	50	6	10.5	35.5	31.9	32.4
60	150	50	6	29.6	65.9	53.8	52.2
120	150	50	6	50.2	75.1	68.5	59.8
240	150	50	6	50.7	75.6	67.5	60.4
720	150	50	6	50.2	76.1	68.0	60.9

Dosage	Agitation Speed	Time	pH	CNF	CNF-Al	CNF-Ti	CNF-Fe
mg	rpm	min		Removal %	Removal %	Removal %	Removal %
10	150	120	6	15.0	51.7	44.6	16.7
50	150	120	6	50.2	78.6	73.6	63.9
100	150	120	6	69.3	86.2	82.7	71.5
150	150	120	6	74.3	95.4	92.3	87.8
200	150	120	6	79.3	100	95.4	92.3
250	150	120	6	82.6	100	100	100
300	150	120	6	85.9	100	100	100
350	150	120	6	95.4	100	100	100
400	150	120	6	100	100	100	100

Table A.8 4-Chlorophenol removal % by raw and Modified FA

	Time	Dosage	Agitation speed	FA	FA-Al	FA-Ti	FA-Fe
pH	(min)	(mg)	(rpm)	Removal %	Removal %	Removal %	Removal %
3	120	50	100	8.5	42.1	35.0	19.2
4	120	50	100	17.5	53.8	40.6	35.0
5	120	50	100	20.6	64.9	59.8	39.5
6	120	50	100	32.1	73.0	67.5	59.8
7	120	50	100	29.6	69.0	62.4	52.7
8	120	50	100	21.1	57.3	37.5	33.5

Agitation Speed	Time	Dosage	pH	FA	FA-Al	FA-Ti	FA-Fe
rpm	(min)	(mg)		Removal %	Removal %	Removal %	Removal %
50	120	50	6	10.5	51.7	51.7	34.5
100	120	50	6	32.1	73.0	67.5	59.8
150	120	50	6	44.2	74.1	73.6	65.9
200	120	50	6	44.7	73.6	72.5	66.4
250	120	50	6	43.7	-	-	-

Time	Agitation Speed	Dosage	pH	FA	AF-Al	FA-Ti	FA-Fe
min	rpm	(mg)		Removal %	Removal %	Removal %	Removal %
10	150	50	6	1.5	12.1	10.1	4.0
30	150	50	6	10.0	33.5	21.8	21.8
60	150	50	6	28.6	63.4	42.6	42.1
120	150	50	6	44.2	70.5	67.5	48.73
240	150	50	6	44.7	71.0	66.4	47.7
720	150	50	6	44.2	70.5	67.0	48.2

Dosage	Agitation Speed	Time	pH	FA	FA-Al	FA-Ti	FA-Fe
mg	rpm	min		Removal %	Removal %	Removal %	Removal %
10	150	120	6	14.5	48.7	42.1	21.3
50	150	120	6	44.2	74.1	62.4	37.5
100	150	120	6	57.2	82.7	75.1	47.7
150	150	120	6	67.2	89.3	81.2	71.5
200	150	120	6	77.3	93.9	89.3	82.2
250	150	120	6	80.6	98.0	96.4	91.3
300	150	120	6	88.9	100	100	100
350	150	120	6	90.4	100	100	100
400	150	120	6	96.4	100	100	100
500	150	120	6	100	100	100	100

APPENDIX B

Calculations of the Chemical Materials

1) Aluminum Nitrate(solid):

$$\frac{375.13(\frac{gm}{mol})}{x} = \frac{26.981(\frac{gm}{mol})}{0.25(gm)}$$

x =3.475 gm of (AL $(No_3)_3.9H_2O$)

2) Titanium isoprpoxide (liquid):

$$\frac{284.22(\frac{gm}{mol})}{x} = \frac{47.867(\frac{gm}{mol})}{0.25(gm)}$$

x =1.48 gm of (Ti -isoprpoxide)

Density of the Ti-isoprpoxide =0.96g/ml

The required volume of Ti –isopropoxide (ml) = $\frac{1.48gm}{0.96(gm/ml)} = 1.55\ ml$

3) Ferric Nitrate (solid):

$$\frac{404(\frac{gm}{mol})}{x} = \frac{55.847(\frac{gm}{mol})}{0.25(gm)}$$

x =1.809 gm of (Fe $(NO_3)_3.9H_2O$)

Table B.1: The Percentages of Impregnation

Adsorbent	Metal	Impregnated Metals (%)
AC	Al	83.0
CNT	Al	87.0
CNF	Al	85.0
FA	Al	90.0
AC	Fe	89.0
CNT	Fe	85.0
CNF	Fe	88.0
FA	Fe	89.5

APPENDIX C

Table C.1: Materials for Experiment.

NO	MATERIALS
1	Sample Adsorbents ▪ Raw and Modified AC. ▪ Raw and Modified CNT. ▪ Raw and modified CNFs. ▪ Raw and modified FA.
2	Stock phenol solution.
3	Stock 4-Chlororphenol solution.
4	1.0M Sodium Hydroxide.
5	1.0M Nitric Acid.
6	Deionizer Water.
7	Ethanol (purity 98%)
8	Aluminum Nitrate, Titanium isoprpoxide and Ferric Nitrate

APPENDIX D

Table D.1: Equipment for the Experiment.

No	Equipments
1.	Inductively Coupled Plasma Mass Spectrometer (ICP-Ms)
2.	Scanning Electron Microscopy (SEM)
3.	Energy Dispersive X-ray Spectroscopy (EDX)
4.	Thermo Graphitic Analysis (TGA)
5.	UV- VIS-Spectrophotometer
6.	Mechanical shaker
7.	Nano Coating Device
8.	Magnetic stirring Heater
9.	Sonicator.
10.	Balancer
11.	pH indicator
12.	1000 ml volumetric flask
12.	100ml Conical flasks

APPENDIX E

Experimental Figures

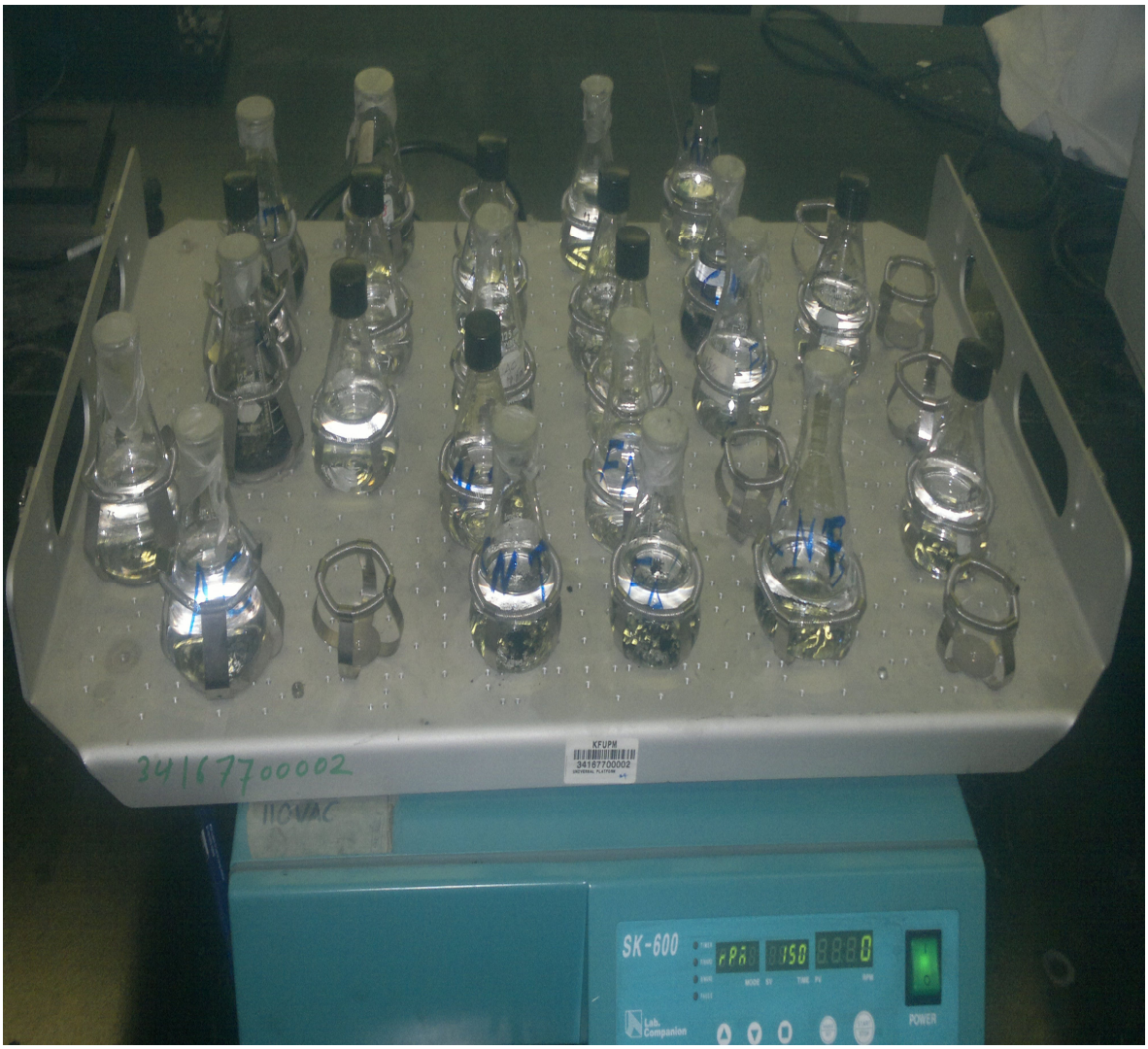


Figure E.1 Photograph of Mechanical shaker Instrument

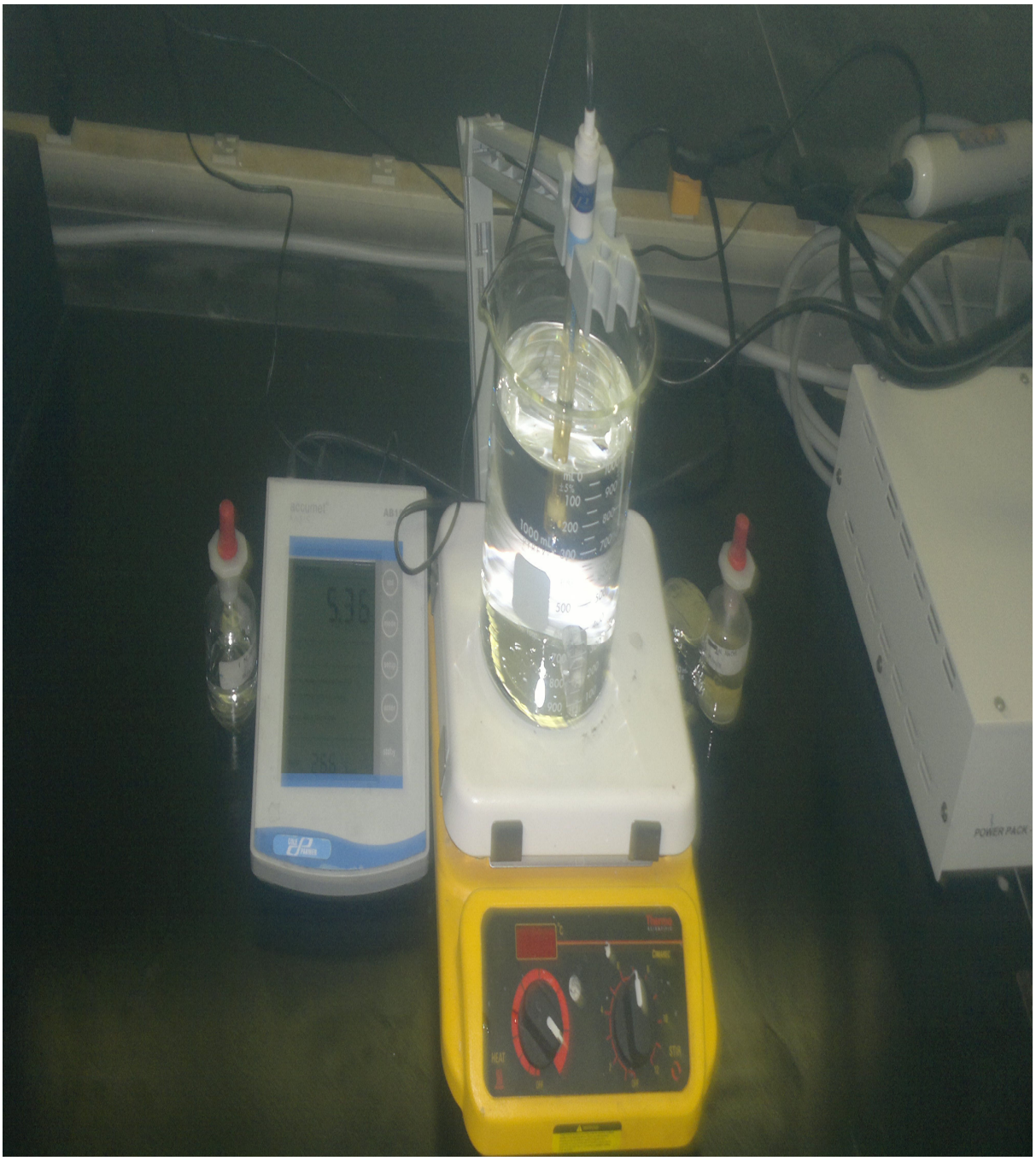


Figure E.2 Photograph of pH Indicator

Figure E.3 Photograph of the Sonicator

Figure E.4 Photograph of the Deionizer water Instrument

Figure E.6 Photographs of the (SEM) and (XRD)

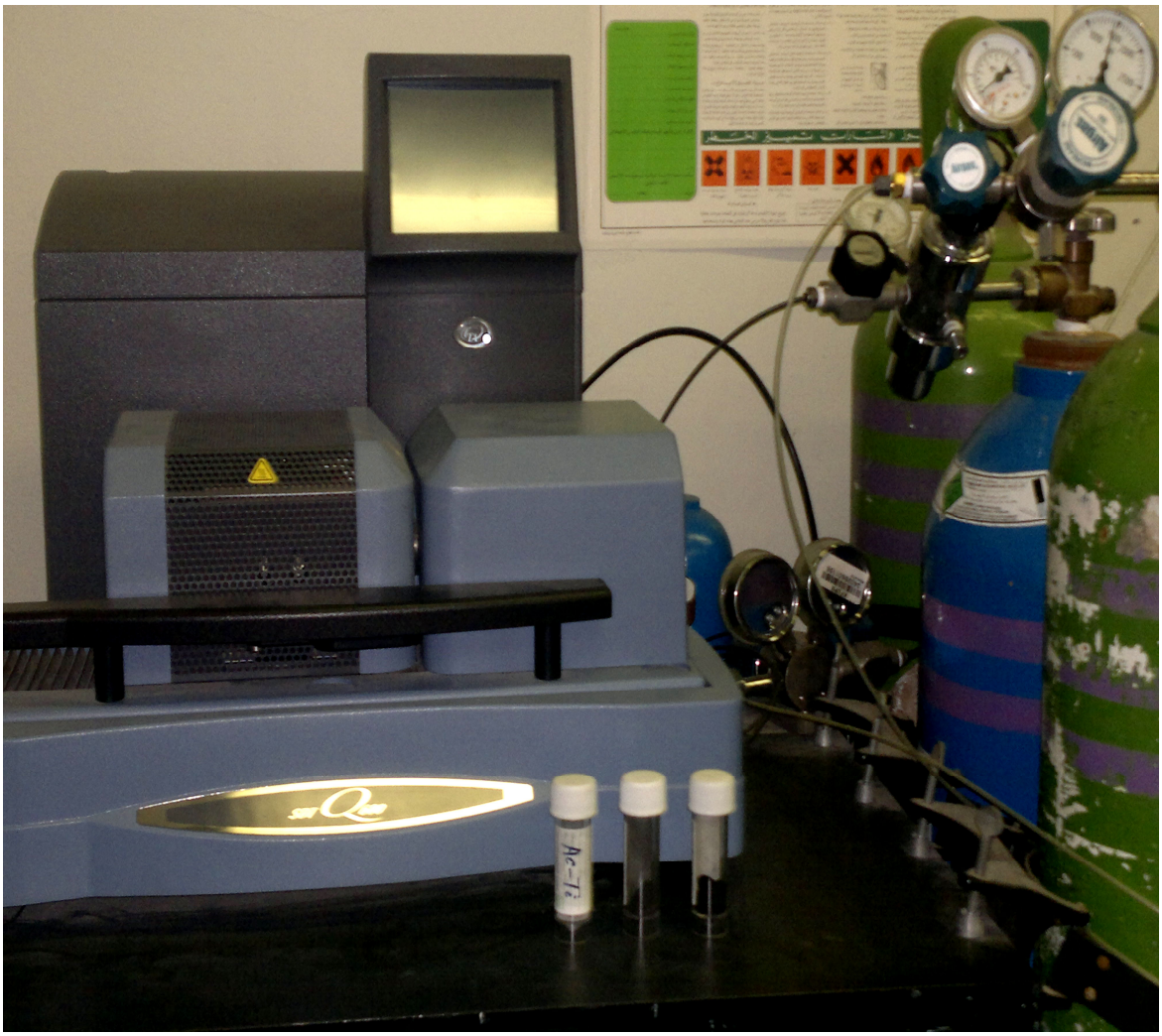


Figure E.7 Photograph of (TGA) Instrument.

Figure E.8 Photograph of nano coating device

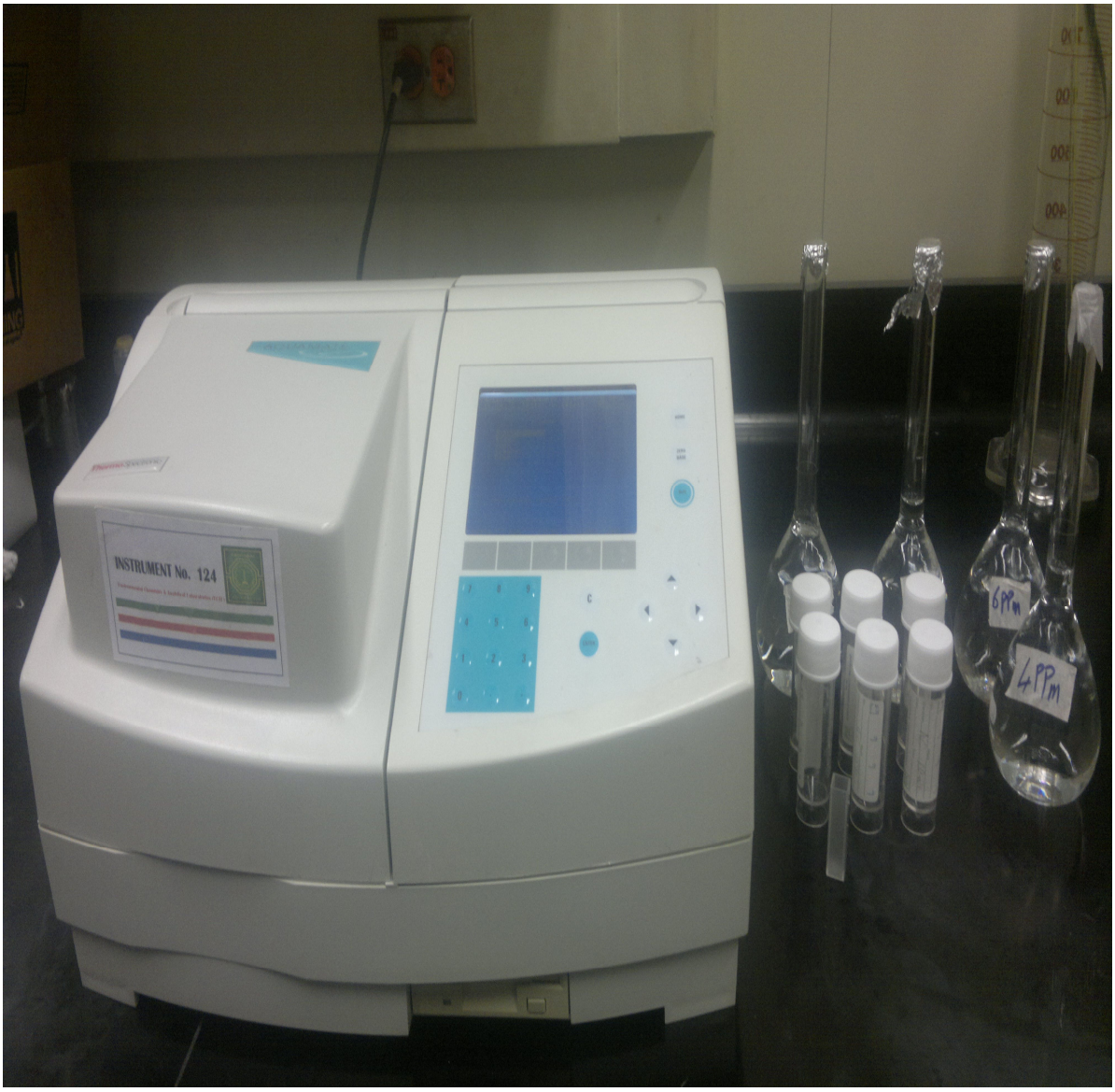
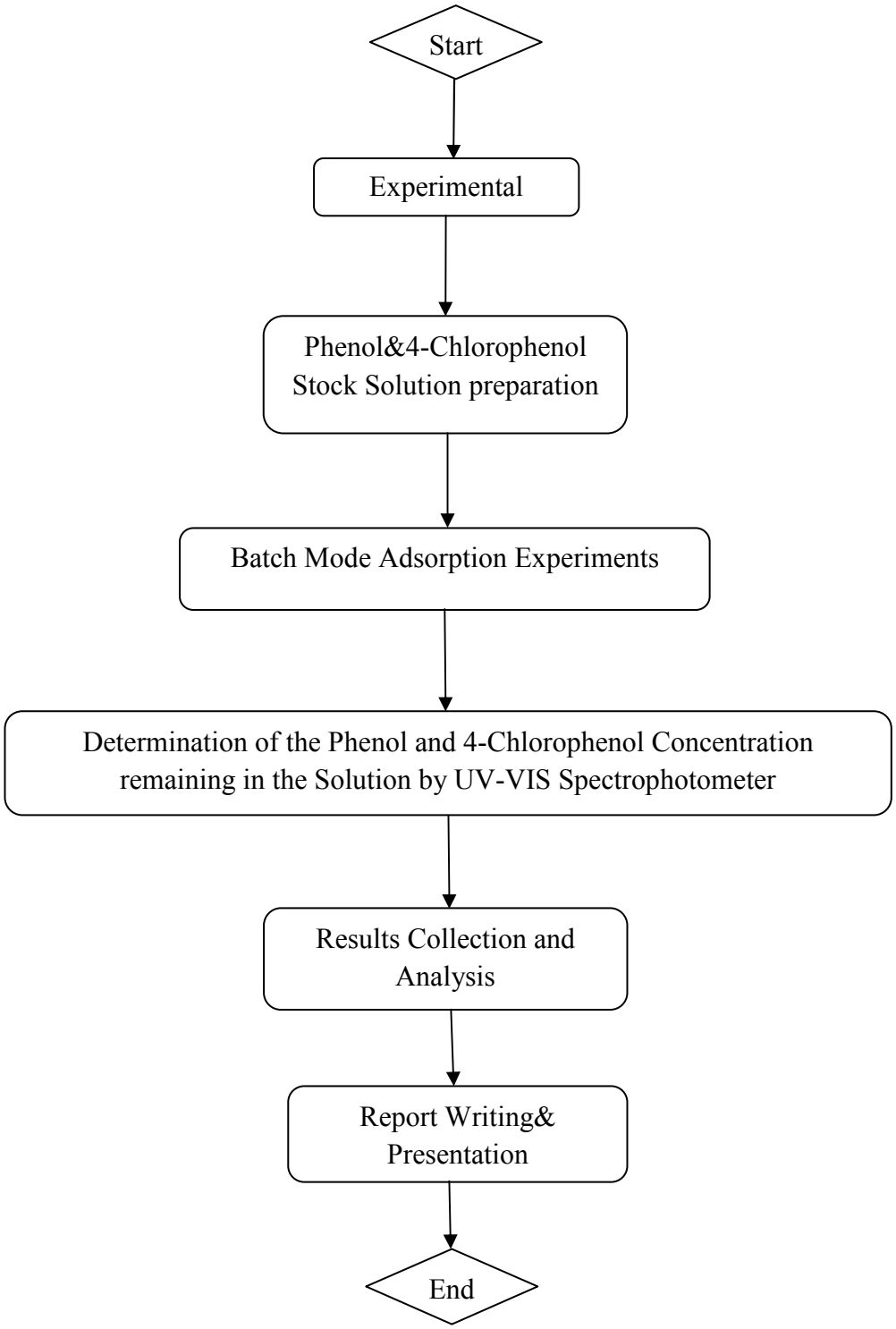


Figure E.9 Photograph of the UV- VIS- Spectrophotometer

APPENDIX F

Experimental Flowchart for Final Year Project



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